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BEHAVIOR OF CUP CURRENT METERS UNDER CONDITIONS NOT COVERED BY STANDARD RATINGS

BY FRED C. SCOBEE,

Irrigation Engineer, Office of Experiment Stations

Experience gained in taking a long series of canal measurements led the writer to believe that the conditions met in field measurements of the flow of water in open channels by the use of current meters varied so widely from those under which the meters are rated as to render inaccurate to an appreciable degree the results of field measurements computed on the basis of the ratings usually made. For the purpose of determining this point, a series of experiments was made, with the results reported here.

The meter used was the small Price meter commonly used for determining the velocity of flowing water. The usual practice in rating a current meter is to make the tests for all velocities with the meter at the same distance beneath the surface of the water—from 1 to 2 feet—and far enough from the sides and bottom of the channel or reservoir in which the rating is made and from all obstructions to be beyond their influence. In addition, the meter is usually held quite rigidly in a horizontal position, on either a rod or a cable. In field use, on the contrary, the meter is used from the surface to the bottom and close to the sides of the channels throughout the entire range of depths found in the streams measured; and in high velocities there is a strong tendency for the meter to be forced out of its horizontal position. The tests discussed here were made for the purpose of determining whether the standard ratings, made as described, hold good when the meter is held near the surface of the water or near the sides or bottom of the channel or out of the horizontal. Further tests were made to determine the effect of the movement of the meter in the water when the "integration" method is used and also the effect of dulling the pivot bearing of the meter.

On September 5 and 6, 1913, a series of runs was made at the meter rating station of the California Development Co., at Calexico, Cal.¹

¹ For a detailed description of this station, see Allison, J. C., Selling water by current meter measurement, in *Engin. News*, v. 69, no. 2, 1913.

This station consists of a car, measuring accessories, and a concrete trough with a level bottom. The trough is 2 feet wide on the bottom and 3 feet deep, with side slopes of 1 to 1. At the time the experiments were made it was carefully cleaned of silt and débris and filled about three-fourths full with fresh ditch water carrying a rather high percentage of silt.

The experiments at Calexico consisted of runs with the meter on a rod and held horizontal at a depth of 1 foot below the surface of the water, practically reproducing the conditions under which it was rated, runs with the meter tipped upward and downward at various angles, runs with the pivot dulled, runs with the meter held close to the side walls of the trough, and runs with the meter just clearing the bottom of the trough. The results of these experiments, plotted to logarithmic scale, are shown in figure 1.

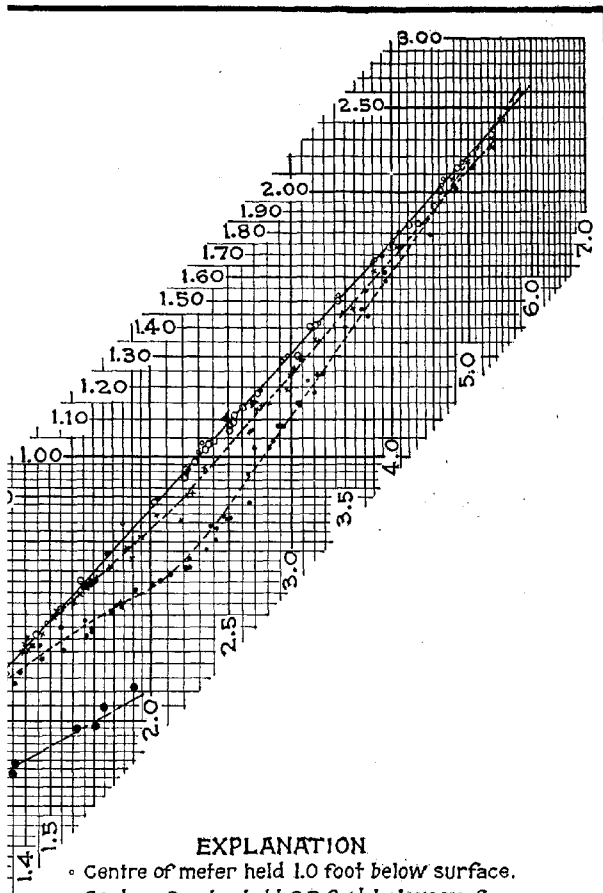
The meter used was rated at Chevy Chase Lake, near Washington, D. C., during the first half of May, 1913, by the United States Bureau of Standards and had been in use throughout the summer. The points developed by this original rating for the runs made with the meter equipped with a single-point contact head, as it was during the experiments at Calexico, are also shown in figure 1, for comparison with the Calexico results. The curve shown on the figure represents the results of the original rating.

For the meter submerged 1 foot, the rod held vertical, and with the pivot in good condition the points are as close to the curve of the original rating as a majority of the points in the original rating, but are all on one side of the curve, indicating that the meter was slightly faster after several months' use than at first, but the difference is so slight as to be negligible.

The runs made with the meter tipped out of the horizontal position indicate that the meter does not run true to the standard rating curve. Not enough runs were made under these conditions to develop curves, but the results indicate clearly that it is very important to keep the meter horizontal.

The runs with the meter held close to the sloping sides of the trough gave points on both sides of the standard rating curve, but indicate that the meter runs true to the rating curve under these conditions. This is shown also by experiments at Cornell University, which will be discussed later.

The runs with the meter just clearing the bottom of the concrete channel show that a correction is necessary when the meter is so used in practice. When plotted on a natural scale, the data shown in figure 1 indicate that, with the meter used, the water would actually flow about 0.06 foot per second faster than indicated by the velocity of the meter. On a natural scale the curve for the meter held at the bottom was quite parallel to the standard curve and 0.06 foot per second slower.



EXPLANATION

- Centre of meter held 1.0 foot below surface.
- ◊ Centre of meter held 0.3 foot below surface.
- ×
- Centre of meter held 0.1 foot below surface.
- Centre of meter held at surface.
- Centre of meter held 1.0 foot below surface, with open ends of cups close to vertical wall.
- ▲ Centre of meter held 1.0 foot below surface, with closed ends of cups close to vertical wall.

d in the rating of a new cup meter at the hydraulic laboratory of Cornell University by holding the meter nearer the sides of the channel than is done in the usual rating.

For the experiments made with a dulled pivot the pivot was roughly rounded on a carborundum wheel to a curve of about the same radius as the shaft—far duller than probably would ever be used in actual practice, as the wheel developed facets. The experiments with the very dull pivot show that for velocities of water greater than 1 foot per second the sharpness of the pivot is immaterial, the points determined by the experiments being closer to the standard curve than most of those from which this curve was developed. As might be expected, the added friction due to the rounding of the pivot has more influence in low velocities, and the meter is a little slow under these conditions.¹

On November 29 and December 1, 1913, the writer made experiments in the concrete channel of the hydraulic laboratory of Cornell University, with a new meter of the same type as that used in the canal measurements during the summer and in the Calxico experiments. The results of these runs are plotted to logarithmic scale in figure 2.

These experiments indicate that for depths below the surface of 0.3 foot or greater the meter runs true to the standard-rating curve at least within the range of velocities covered, which did not exceed 6 feet per second. When the center of the meter is less than 0.3 foot from the surface, the points indicate a peculiar behavior. With the center 0.2 foot below the surface the meter velocities followed the standard curve until a velocity of about 1.5 feet per second was reached. At this velocity the surface of the water above the meter starts to break up and the rating curve leaves the standard curve, as shown by the dash-and-dot line in figure 2, but it did not intersect the standard curve again within the range of the experiments.

With the center of the meter submerged just 0.1 foot the curve leaves the standard curve at a lower velocity—about 1.15 feet per second—as is to be expected. The influence appears to reach a maximum at a velocity of about 2.2 feet per second, at which point the actual water velocity is about 0.45 foot per second higher than the revolutions of the meter would indicate on the basis of the standard curve. As the velocity increases, the two curves come closer together until the curve for the 0.1 foot depth appears to cross the standard curve at a velocity of about 5.5 feet per second. The writer can account for this strange action only on the theory that by the time this velocity is reached the entire surface of the water in the vicinity of the meter has become shattered, and enough wind pressure operates against the cups to turn the meter even faster than would be the case when submerged 1 foot. If a cup meter is held in the air, the great influence of a very slight wind is at once manifest.

¹ In correspondence, Mr. V. M. Cone, Irrigation Engineer, Office of Experiment Stations, points out "that the ratings did not change materially on those pointed bearings if they were merely dulled, but the big trouble came when using the meter in comparatively swift water. There was a tendency for the turbine to lift, throwing the conical bearing upward, and very often a shoulder would be cut on the sloping face. Whether this is due to a mechanical defect in the instrument or to grit getting into the bearing I do not know, but wherever that groove or shoulder was cut the rating was very materially changed."

Merely to make the data complete rather than to duplicate conditions of field use, the meter was again raised in the water until the center plane of the cups was just at the water surface. The curve for this condition shows that the meter runs slow when a low velocity is reached, and the difference between the curves rapidly becomes greater within the range of the experiments.

Murphy, in the report of his experiments at Cornell University,¹ also pointed out the fact that the Price meter does not run true to standard rating curve when held near the surface. He compared the velocity as indicated by the meter with that of a surface float operated simultaneously in running water. His general deduction was that this type of meter does not run true to standard curve when operated at depths less than 0.5 foot below the surface. The writer found, however, by actu-

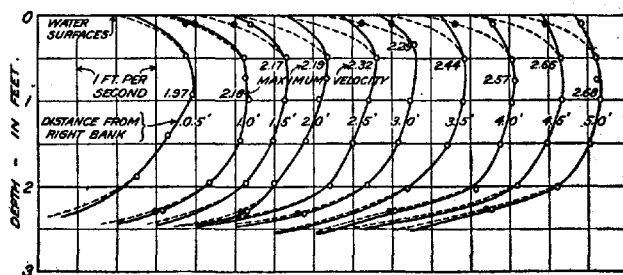


Fig. 3.—Vertical velocity curves, showing error due to using standard rating for points near the surface and bottom, Orr ditch, Nevada.

ally rating the meter at various depths, that the behavior of the meter becomes normal somewhere between depths of 0.2 and 0.3 foot below the surface.

A concrete example of the difference in results obtained when the proper correction for surface and bottom velocities is applied follows:

The Orr ditch at Reno, Nev., was measured with a current meter, using the vertical velocity-curve method. The ditch channel was lined on the sides with rubble masonry. This channel was 10 feet wide and of nearly rectangular section. The vertical velocity curves for the right half of the section are shown in figure 3. The open circles and solid lines give the curves after the proper corrections have been applied to the velocities for the surface and the bottom. The dots and broken lines show the form the curves would have assumed if no corrections had been applied. The curves for the other half of the section were quite similar to these. The verticals were spaced 0.5 foot apart. The total discharge indicated by the solid curves is 45.80 second feet, while that

¹ Murphy, E. C. Accuracy of stream measurements. U. S. Geol. Survey, Water-Supply and Irrig. Paper No. 95, 1904, p. 90.

indicated by the original curves, which followed the dotted lines of figure 3, is 44.82 second feet, which is 2.14 per cent less than the discharge computed with proper corrections applied. The mean velocity indicated by the solid curves is 1.76 feet per second. As influenced by the broken portions, it is 1.72 feet per second. For a given depth and a given mean velocity the difference in results with and without the proper corrections will vary approximately as the width of the channel, but for a given

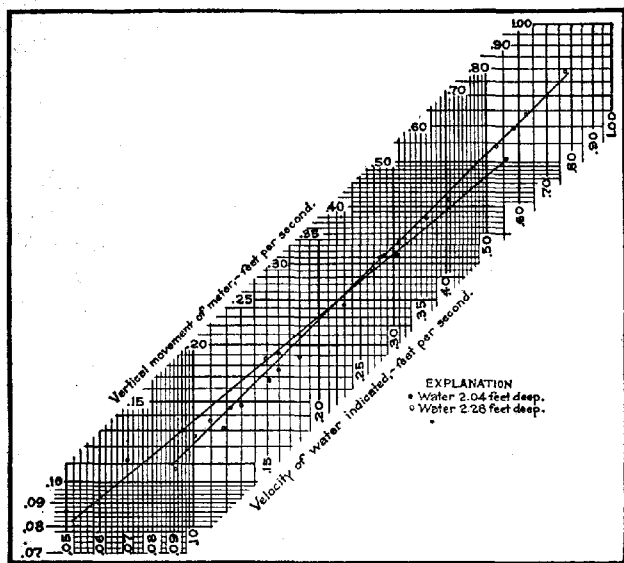


FIG. 4.—Curves on logarithmic scale, showing relation between rate of vertical movement of a cup meter and velocity of water as indicated by the revolutions of the turbine due to vertical movement in still water.

width of channel the difference approximates a constant quantity without regard to depths and velocities rather than a percentage difference.

The main point the writer desires to bring out is that a cup current meter should be actually rated at the surface and bottom of the channel if it is to be operated at these points in making discharge measurements. From the various rating tables thus developed the proper interpretation of the speed of the meter can be recorded.

Runs with the meter held close against the vertical concrete wall of the channel indicate that the meter runs true to the standard curve, but disregards the cycloidal motion of the water. As the rating car passed to and fro over the channel, the meter was held close to the same wall, thus bringing the open and closed sides of the turbine, alternately, next to the wall.

For the purpose of determining the influence on a meter of the vertical motion in the water when the vertical integration method is employed, experiments were made in Lake Tahoe, Cal., on July 20, 1913. During the first 11 runs the meter was operated by the writer's assistant. The surface of the lake was smooth and the water exceptionally clear, so that the meter could be seen plainly. The particular cup which passed under the yoke at the moment of the electrical click was marked, and a definite number of round trips were made from the top of a flat rock 2.04 feet below the surface to the surface and return. By watching the marked cup it was possible to determine the fractional parts of a revolution to within probably one-fifth of a revolution. A slight breeze sprang up later in the day, and the meter was taken to a protected place where the water was clear, 2.28 feet deep, and without a ripple. For the runs made in this depth of water the writer operated the meter.

In order to give a clearer understanding of the plotted results shown in figure 4, information in detail of the separate runs is given in Table I.

TABLE I.—Indicated velocity of water due to vertical movement of cup meter in still waters of Lake Tahoe, Cal.

Run No.	Depth of water.	Number of round trips.	Time.	Number of revolutions.	Vertical movement of meter per second. ¹	Number of revolutions per second.	Indicated velocity of water per second.
	<i>Feet.</i>		<i>Seconds.</i>		<i>Feet.</i>		<i>Feet.</i>
1	2.04	1	69.4	0.0	0.053	0.000	0.000
2	2.04	4	77.0	4.5	.191	.038	.160
3	2.04	4	60.4	5.5	.244	.091	.230
4	2.04	4	85.8	5.0	.176	.060	.160
5	2.04	3	84.8	2.5	.150	.037	.095
6	2.04	3	98.8	1.7	.112	.017	.070
7	2.04	3	128.6	1.2	.086	.009	.050
8	2.04	5	48.8	7.2	.377	.148	.360
9	2.04	5	36.4	8.7	.500	.239	.560
10	2.04	9	105.4	13.2	.314	.135	.307
11	2.04	2	44.2	2.4	.167	.054	.152
12	2.28	3	57.2	3.8	.218	.067	.180
13	2.28	3	49.4	4.5	.309	.111	.280
14	2.28	3	40.2	4.6	.311	.114	.285
15	2.28	3	67.2	3.6	.186	.054	.149
16	2.28	2	61.2	2.1	.156	.034	.110
17	2.28	2	56.6	2.5	.147	.044	.130
18	2.28	2	65.8	2.1	.126	.032	.101
19	2.28	5	50.0	8.5	.416	.170	.408
20	2.28	7	49.0	12.3	.594	.251	.585
21	2.28	5	38.5	8.7	.540	.226	.530
22	2.28	7	37.0	13.5	.788	.338	.778
23	2.28	8	52.2	14.0	.637	.270	.625
24	2.28	2	63.4	2.5	.131	.039	.118
25	2.28	2	77.8	2.2	.107	.028	.091
26	2.28	3	37.4	4.7	.314	.126	.310
27	2.28	3	36.2	3.7	.145	.043	.131
28	2.28	4	88.6	6.0	.188	.068	.180

¹ For one round trip the meter moves 0.4 foot less than twice the measured depth of water.

The curves plotted to logarithmic scale are based on points whose ordinates represent the velocity in feet per second at which the meter was drawn through the water (column 6), and the abscissas represent the velocity of water indicated by the number of revolutions generated

¹ By "open side of turbine" is meant the side on which the open ends of the cups are upstream.

by the vertical movement on the basis of the standard rating (column 8). The two curves show a slight difference, probably due to two causes: First, the difference in depth of the water and the consequent difference in the relation between the number of turns at top and bottom and the distance through which the meter travels. Second, a difference in the manner in which different men operate the meter. For the higher rates of movement of the meter the points for the curve appear quite consistent. This is due to the fact that the turbine rotates all the time, even in still water, when the vertical movement is faster than about 0.2 foot per second. Below that velocity of movement the turbine rotates part of the time and remains at rest part of the time. It was noticed that the turbine rotates part of a revolution when the motion was changed from up to down, and vice versa. At these points the turbine rotated a little and then came to rest again and remained so while the meter was being moved in a vertical direction to the next turning point.

A general deduction from these curves is to the effect that all vertical movement of the meter tends to turn the wheel in the same direction as does the flowing water. For the slower movements of the meter this tendency is not sufficient to overcome the internal friction in the meter, but, when it is operated in running water, the water already has overcome this internal friction, and the force due to the vertical movement of the water is still available to turn the wheel and thus cause it to over-register.

Again referring to figures 1 and 2, it appears that a cup meter under-registers at all points nearer the surface than about 0.3 foot and also while very near the bottom. Therefore, in a process of vertical integration with a cup meter there is a tendency to overregistration at all times due to the vertical motion, and a tendency to underregistration while the meter is passing from about 0.3 foot below the surface up to the surface and back to that point and while near the bottom. These compensating tendencies account for the fact that if the meter is moved very uniformly and very slowly the integration method gives results as close to actual discharge as it does.

EREMOCITRUS, A NEW GENUS OF HARDY, DROUTH-RESISTANT CITROUS FRUITS FROM AUSTRALIA

By WALTER T. SWINGLE,

*Physiologist, in Charge of Crop Physiology and Breeding Investigations,
Bureau of Plant Industry*

A survey of the plants belonging to the orange subfamily (Citrateae), undertaken in the hope of finding new material for use in breeding, has brought to light a citrous plant which combines in some degree the winter dormancy of the kumquat and the absolute cold resistance of the trifoliolate orange. This is the Australian desert kumquat, originally described as *Triphasia glauca* Lindl. and now called *Atalantia glauca* (Lindl.) Benth. by most botanists.

A study of the reports of the early Australian exploring expeditions has shown that this plant is undoubtedly the most cold-resistant of all the evergreen citrous fruits, that it is also drouth-resistant, and yields an edible, though small, kumquat-like fruit. With these qualities it combines a high degree of winter dormancy.

An examination of the scanty material of this plant preserved in the herbaria of Europe and America and a study of living plants now growing in the greenhouses of the Department of Agriculture at Washington, D. C., show that its relationships have been misunderstood by botanists. When first described it was wrongly put into the genus *Triphasia* and is still out of place in the genus *Atalantia*, to which it is now referred. As a matter of fact, the Australian desert kumquat is much more closely related to *Citrus* than are either of the genera just named. It is most closely related to the Australian species of *Citrus* and, like them, can in all probability be hybridized with the commonly cultivated species of *Citrus*. It can be grafted readily on the common citrous stocks.

The Australian desert kumquat is in many ways unique. It is the only member of the subfamily Citrateae that shows marked adaptation to desert climates. It is a gray-green shrub or small tree, looking not unlike a large, thorny sage bush, having leaves centric in structure, with appressed hairs, stomates, and a very thick-walled epidermis on both surfaces and palisade tissue just beneath. The slender, usually spiny twigs (fig. 1) are also gray-green and have stomates situated at the bottom of deep pits. In all of these and in some other characters the plant shows the outward signs of a profound adaptation to withstand the extreme heat and dryness of a desert climate.

Because of these unique structural peculiarities and because of decided differences in the number, arrangement, and character of the floral

organs, it seems necessary to create a new genus to include this interesting plant.¹

Eremocitrus Swingle.

The genus *Eremocitrus* resembles *Citrus* in the structure and appearance of the fruits; it differs from it (1) in the leaves which have on both surfaces palisade cells, sunken

stomates, and appressed few-celled hairs; (2) in the 4- to 5-merous flowers, with free stamens and a 4- or 5-celled ovary, with 2 ovules in each cell.

The leaves are gray-green, thick and leathery, and markedly pellucid punctate; they are nearly alike on both sides, having four ventral and two dorsal layers of palisade cells, sunken stomates, an epidermis with a thick cuticle, and scattered few-celled appressed hairs on both surfaces. The spines are usually long and slender, but are sometimes wanting, especially on fruiting branches of old trees. They occur singly in the axils of the leaves. The twigs are gray-green, slender, very slightly angled when young, with scattered stomates at the base of deep, narrow pits, and two or more layers of palisade cells below the very thick-walled epidermis. The flowers

occur singly or two or

three together in the axils of the leaves and are borne on slender pedicels about as long or slightly longer than the petals. (See fig. 1.) The calyx is 3- to 5-lobed; the petals, four or five, rarely three in number, are more or less narrowed at the base;



FIG. 1.—*Eremocitrus glauca*: Twigs from a syntypic specimen collected by T. L. Mitchell, near Forestvale, Queensland, Australia, on October 17, 1846; from Gray Herbarium. A, Spiny twig showing a single flower; B, spineless sterile twig; natural size. C, tetramerous flower seen from the side. X5. Drawn by Theodor Holm.

¹*EREMOCITRUS* gen. nov. (*Asyris* deserta + *Citrus*).—Genus *Citro* affinis, foliis utrinque stomatibus pilisque instructis; floribus 4- vel 5-meris, staminibus liberis, ovario 4- vel 5-loculare, loculis 2-spermis.

Folia cinereo-viridia, crassiuscula, pellucido-punctata, mesophyllo centrico, utrinque stomatibus et pilis adpressis, pauci-cellularibus instructa. Spinae in axillis foliorum singulae, interdum in ramis veteris carentes. Flores in axillis foliorum singulae vel paucae, pedicellatae, 4- vel 5-merae; petala basi angustata; stamina libera, numero petalorum quadruplo; ovarium 4- vel 5-loculare, ovulis in locula binis; stylus breviusculus, crassus, caducus. Fructus ovalis vel pyriformis, cortice ut in *Citro* carnosus, glandulis oleiferis instructa; pulpa vesiculari acida, vesiculis subglobosis pedicellatis. Semina parva, 5 mm. longa; testa dura rugosa; cotyledones hypogaeae; folia primitiva cataphylla.

Arbustula vel arbor parva, spinosa.

Species typica et unica, *Triphasia glauca* Lindl.

the stamens are normally four times as numerous as the petals, with the filaments free. The ovary is obovate, with a rather thick, subcylindric, caducous style, 4- or 5-celled, with two ovules in each cell; the disk is small. The fruits are $1\frac{1}{2}$ to $2\frac{1}{4}$ by $1\frac{1}{4}$ to $1\frac{1}{2}$ cm.—smaller than those of any known species of *Citrus*—subglobose, oval or somewhat pyriform, with a thin, fleshy peel, like that of a lime, covered with oil glands. The pulp is vesicular, sour, and juicy. The pulp vesicles, which separate easily in the ripe fruit (fig. 2, A-D), are subglobose, and are borne on slender stalks. The seeds are small (5 to 6 by 3 to 4 by $2\frac{1}{2}$ to 3 mm.), pointed ovate, yellowish gray with a hard testa, irregularly verrucose and furrowed in a longitudinal direction. (See fig. 2, E.) The cotyledons are plano-convex, remaining hypogeous in germination; the postcotyledonary leaves are slender cataphylls (fig. 3).

This monotypic genus is based on *Triphasia glauca* Lindl., native to the drier parts of northeastern Australia.

RELATIONSHIPS

Eremocitrus is most nearly related to the three aberrant Australian species of *Citrus*, *C. australis* Planch., *C. australasica* F. Muell., and *C. Garrowayi* F. M. Bail., and agrees with them in having free stamens, subglobose pulp vesicles, and the first postcotyledonary leaves of the young seedlings reduced to cataphylls. It differs from these Australian species of *Citrus* in having gray-green leaves, with palisade cells, stomates, and curious appressed hairs on both surfaces, and also in having the stomates of the twigs situated at the base of pits, in the usually 4-merous flowers, and in the much smaller fruits with only one or two seeds in a segment.

Eremocitrus resembles the kumquat (*Citrus japonica* Thunb.) in being a shrub bearing very small fruits and in its physiological adaptations to secure extreme winter dormancy. The kumquats differ decidedly from it in having usually 5-merous flowers, polyadelphous stamens, and a 5- or 6-celled ovary, short-stalked, fusiform pulp vesicles, and bifacial glabrous leaves. *Eremocitrus* shows little affinity to any other species of *Citrus*.

From true *Atalantias*, such as *A. monophylla* (Roxb.) DC. and *A. citrioides* Pierre, having 2- to 4-celled fruits with pulp vesicles, *Eremocitrus* differs in having the stamens four times as numerous as the petals instead of twice as numerous. It also differs markedly from *Atalantia* in the structure of the leaves. It differs from the African cherry oranges (*Citropsis* spp.) in having simple leaves, two ovules in each cell of the ovary, stalked pulp vesicles, and in many anatomical characters.

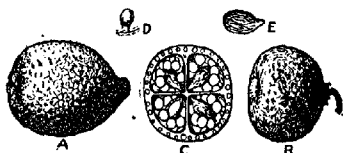


FIG. 2.—*Eremocitrus glauca*: Fruits and seed from Tambo, Queensland, Australia (S. P. I. No. 29537, James Pink, January, 1912). A, large pyriform fruit, natural size; B, small oblate fruit, natural size; C, cross section of a 4-celled fruit, showing four seeds and numerous pulp vesicles, natural size; D, a single, short-stalked pulp vesicle. X2; E, seed, showing rugose testa. X $\frac{1}{2}$. Drawn by M. W. Gill.

In its fundamental morphological characters, *Eremocitrus* probably represents fairly accurately the ancestral type from which were derived

the Australian species of *Citrus*. This ancestral type has been, however, profoundly modified by the superposition of many anatomical and physiological characters acquired as a result of a long-continued struggle for life in a desert climate.

Only one species of *Eremocitrus* is known:

Eremocitrus glauca (Lindl.), n. comb.

Triphasia glauca Lindl., ex T. L. Mitch., 1848. Jour. Exped. Trop. Austral. p. 353. London.

Alalantia glauca Benth., 1863. Fl. Austral. v. 1, p. 370. London.

Illus., W. S. Campbell, 1899, in Agr. Gaz., N. S. Wales, v. 10, p. 1168, fig. 5, sub. nomen *Citrus australis* (sterile twigs); Fairchild, 1912, in U. S. Dept. Agr. Yearbook, 1912, pl. 45, fig. 1 (fruits only).

This species, the desert kumquat, desert lemon, or desert lime of the Australian pioneers, is a shrub or small tree sometimes attaining a height of 15 feet and a diameter of 6 inches (Maiden, 1889, p. 379).¹ When young, the branches are very spiny and the leaves are very narrow. As the tree gets older, the leaves become broader and more abundant and the spines are much reduced or entirely wanting (Campbell, 1899, p. 1168, fig. 5).

The leaves of mature plants are oblong linear or elongate cuneate, bluntly rounded, retuse or emarginate at the tip, with undulate entire margins, 25 to 45 by 4 to 10 mm., mostly 30 to 40 by 6 to 8 mm. They show on both surfaces minute (about $\frac{1}{10}$ mm. long), scattered, appressed few-celled hairs, with a warty cuticle. The leaves are paraheliotropic (standing more or less on edge), very thick, prominently glandular dotted, and taper gradually into very short wingless petioles.

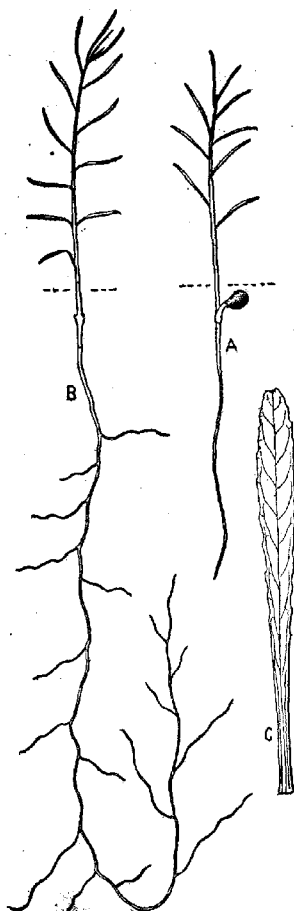


FIG. 1.—*Eremocitrus glauca*. Seedling plants grown from seed from near Chinchilla, Queensland, Australia (S. P. I. No. 20660). A, a young seedling with hypogeous cotyledons still inclosed in the seed coats, natural size; B, an older seedling with a very long taproot, natural size; C, a cataphyll. X5. Drawn by Theodor Holm.

¹ Bibliographic citations in parentheses refer to "Literature cited," pp. 99-100.

The spines, which are always single, are slightly to one side of the axil of the leaf and are usually very slender, 2 to 4 cm. long and only $1\frac{1}{2}$ to 2 mm. in diameter. On old trees, especially on fruiting branches, they are often wanting.

The flowers are borne either singly or in groups of two or three in the axils of the leaves on new growth, as in *Citrus*. The pedicels are slender, 4 to 6 mm. long. The calyx is 3- to 5-lobed, sparsely hairy, the lobes acute. The petals are four or five (rarely three) in number, somewhat narrowed at the base, and broadly rounded or bluntly pointed at the tip, 4 to 6 mm. long. There are four times as many stamens as petals, usually 16 to 20, rarely 12 (in trimerous flowers); the filaments are slender, about 4 to 5 mm. long. The pistil is borne on a low disk and has an obovate ovary, with a rather thick subcylindric style (fig. 4); the ovary is 4- or rarely 3- to 5-celled; each cell contains two ovules.

The fruits are small, globose, oblate, or sometimes pyriform, $1\frac{1}{2}$ to $2\frac{1}{2}$ by $1\frac{1}{4}$ to $1\frac{1}{2}$ cm., having four (rarely three or five) cells filled with subglobose stalked pulp vesicles. The seeds are oval, yellowish gray, 5 to 6 by 3 to 4 by $2\frac{1}{2}$ to 3 mm., with a tough, longitudinally furrowed, and verrucose testa (see fig. 2). The cotyledons are hypogeous in germination, and the young seedlings produce alternate slender cataphylls which only very gradually become broader and leaf-like. The young spiny plants, even when several years old, usually have only very narrow leaves, differing but slightly from the cataphylls of the young seedlings. (See fig. 3.)

DISTRIBUTION OF EREMOCITRUS

Eremocitrus occurs in northeastern Australia from the Burdekin River, Queensland, latitude 21° S. (Mueller, 1858, p. 150; 1857, p. 169; Gregory, 1857, p. 237), to Dubbo, New South Wales, latitude $32^{\circ} 30'$ S.; also in the coast region near Broad Sound in Queensland, latitude 22° S. Specimens have been examined from the following localities:¹

I. QUEENSLAND.

PORT CURTIS DISTRICT.—Broad Sound. ROBERT BROWN, No. 5343, September, 1802 [?] "*Rutac* ? *suaveolens* Aurantiac. genus 10 and. bacc. polysperma No. 58 desc. not. [?] a Broad Sound. Ad margines dumetis prope Upper Head, Broad Sound." Three twigs, two with flowers, one with young fruits, British Museum; fragment with flowers, Washington, D. C. (National Herbarium); no number, no date, four twigs, two with flowers, two with young fruits, Kew;² fragment in Washington, D. C.



FIG. 4.—*Eremocitrus glauca*: Flower from which petals and stamens have fallen; showing pedicel, calyx (one sepal cut away), disk, ovary, style, and stigma; from a specimen collected by Robert Brown, No. 53, Sept., 1802 (?), Upper Head, Broad Sound, Queensland; in National Herbarium, Washington, D. C. $\times 5$. Drawn by J. M. Shull.

¹ All of the specimens located in herbaria outside of Washington, D. C., were examined and photographed by the writer, and prints enlarged to natural size have been filed in the National Herbarium at Washington, D. C.

² This specimen has a locality label "Broad Sound" in Robert Brown's handwriting, but no other data. It is probably a part of No. 58, as the specimens are similar to those in the British Museum.

(National Herbarium); no number, no date, two sheets of two and three sterile twigs, Paris (Muséum)¹; no number, no date, four sterile twigs, Dahlem.¹

NORTH KENNEDY DISTRICT.—Brigalow Scrub, south of Burdekin River, between latitude 20° and 21° S. FERDINAND MUELLER, no number, October 14 to 30, 1850 (Mueller, 1857, p. 169, 1858, p. 150); three twigs, one with flower and two with fruits, Kew.

SOUTH KENNEDY DISTRICT.—Head of Suttor River. RUTHERLAND, no number, no date [before 1867], two twigs, one with young fruits, one sterile, Kew.

MARANOA DISTRICT.—Dublin County, near Forestvale, between Possession Creek and "Camp 32," near the junction of Maranoa and Merevale Rivers. T. L. MITCHELL, October 17, 1846, three sheets with flowering twigs,² Kew; "Interior of New South Wales, SIR T. L. MITCHELL, Presented 1847," two twigs, one with fruits, British Museum; two twigs, one with flower (see fig. 1), Harvard (Gray Herbarium).

WARREGO DISTRICT.—F. M. BAILEY, no number, no date (before 1911), two twigs, one with flower buds, one sterile, Washington, D. C. (National Herbarium).

In vicinity of Tambo. Collected for JAMES PINK (S. P. I. No. 29537), January, 1911; fruits only (fig. 2; see also Pl. XLV, fig. 1, U. S. Dept. of Agr. Yearbook for 1911), Washington, D. C. (Department of Agriculture Economic Collections, National Herbarium); WALTER T. SWINGLE (C. P. B. No. 7239), February 20, 1914; twigs cut from greenhouse plants grown from seed sent by James Pink, Washington, D. C. (National Herbarium).

DARLING DOWNS DISTRICT.—Lytton County, near Chinchilla. "Growing naturally on the Condamine River, 12 miles from Chinchilla Rly. Station," collected for JOHN WILLIAMS (S. P. I. No. 29660), December, 1910, seeds only, Washington, D. C. (Department of Agriculture Economic Collections, National Herbarium); WALTER T. SWINGLE (C. P. B. No. 7244), February 20, 1914, leafy twigs from plants grown in Department of Agriculture greenhouse from seed sent by John Williams, Washington, D. C. (National Herbarium).

Aubigny County, Dalby. T. L. BANCROFT, no number, no date, "Desert or native kumquat, used by settlers," one twig with flowers, Washington, D. C. (National Herbarium).

Marsh County, Goondiwindi. Collected for J. H. MAIDEN, no number, May, 1912, twig and ripe fruits, Washington, D. C. (National Herbarium); WALTER T. SWINGLE (C. P. B. No. 7522), February 20, 1914, leafy twigs from plant grown in Department of Agriculture greenhouse from seed sent by J. H. Maiden, Washington, D. C. (National Herbarium).

II. NEW SOUTH WALES.

Lincoln County, Dubbo. Collected for J. H. MAIDEN (C. P. B. No. 2901), April 22, 1910, fruits only, Washington, D. C. (National Herbarium).

Finch County, Collarenebri. Collected for J. H. MAIDEN (S. P. I. No. 37808) before March 16, 1914; twigs, leaves, and fruits, Washington, D. C. (National Herbarium).

¹ This material has no original label, but is probably from the same collection as No. 58. All of these specimens show pedicels which have lost the flowers or young fruits.

² *Triphasia glauca* was probably based by Lindley on several syntypes, and it is now difficult to decide which specimen should be designated as the lectotype. One sheet (Herb. Hook., 1867) with four twigs has pencil sketches of the flower parts by "J. H." on a separate sheet. One with two twigs (Herb. Benth., 1842) has a printed label like that on the specimen in Gray Herbarium. The third specimen (Herb. Hook., 1867), also with two twigs, has pencil sketches on the sheet of flower parts and the following notes: "Cal. lobes 4-5, small, unequal imbricate ciliate. Petals 4-5 fleshy, unequal, concave, sessile(?). Stamens 15-20, anthers oblong, sessile(?), 2 loc. 2 longit. rim. Ovary." Above these notes the names "Dodonea," "Celastrus," and "Cfr. Diosma" are written as if in an attempt to identify the plant. On the same sheet are mounted three twigs collected by Mueller on the Burdekin River. These eight twigs in the Kew Herbarium, together with the two in the British Museum and the two in the Gray Herbarium, are probably syntypes.

The first specimens of *Eremocitrus glauca* to be collected in Australia were found by Robert Brown in September, 1802(?), in the thorny brush at Upper Head on the coast region bordering Broad Sound in Queensland and not in its characteristic habitat, the Downs or Brigalow Scrub country, to the west of the coast ranges in southern Queensland and New South Wales. Brown's specimens, the best of which are now found in the British Museum, show unusually abundant leaves and flowers, probably because they were growing in a somewhat moister climate than usual. Either this colony of the desert kumquat represents a slightly different subspecies, or else it is merely a chance colony of the typical form of the species introduced into the coast region by birds or by other means. It differs only in its somewhat luxuriant growth from the desert kumquat of the semiarid scrubs to the west of the coast ranges.

HARDINESS OF THE DESERT KUMQUAT

The accounts of *Eremocitrus glauca* contained in the records of the early exploring expeditions in Australia show it to be native to the semiarid region west of the coastal mountains of Queensland and New South Wales, where drouths are frequent and the temperature often falls low in winter. These records are of interest, as they reveal that this near relative of our citrous fruits has great resistance to cold and drouth.

The first mention as yet found of this plant is in Ludwig Leichhardt's narrative of his expedition from near Brisbane to the Gulf of Carpentaria made in 1844-45 (1847, p. 8, 43, 75, 83, and map). During the months of November and December, 1844, Leichhardt and his party traveled from the Darling Downs, at the headwaters of the Condamine River, about 100 miles northwest of Brisbane, to the Expedition Range, some 300 miles to the northwest. This route was in general parallel to the coast, about 100 to 150 miles inland, and just westward of the coast range for the first half of the distance. The Brigalow Scrub, a dense growth of scrubs and small trees, taking its name from the Brigalow (a species of *Acacia*), whose silvery green leaves give a distinctive appearance to the thickets where it abounds, occupies much of this low plateau region west of the coast ranges, and generally covers the heavy loam soil that overlies the sandstone formation.

Leichhardt, during this portion of his trip, notes repeatedly the presence of a "small orange" or "native lemon." He first found this plant on October 5, 1844, while the party was camping on the Darling Downs.¹ This was in latitude 26° 56' 11" S., and, though the antipodean spring was well advanced (*Eremocitrus glauca* was in flower when seen here), the thermometer had registered 32° F. at sunrise two days previously.

¹"A small orange tree, about 5-8' high, grows either socially or scattered in the open scrub * * *"
(Leichhardt, 1847, p. 8.)

On November 20, in traveling along Robinsons Creek in latitude about $25^{\circ} 30' S.$, he notes (Leichhardt, 1847, p. 43) that:

* * * the country began to rise into irregular scrubby ridges; the scrub generally composed of *Vitex* intermingled with various forest trees. The small orange-tree, which we had found in blossom at the Condamine, was setting its fruit.

The last mention of the plant was made on December 24, while the party was in the region between the Expedition and Christmas Ranges, latitude $24^{\circ} 30'$ to $45' S.$ On that day Leichhardt (1847, p. 83) observed:

Here we passed an extensive Myal forest, the finest I had seen, covering the hilly and undulating country, interspersed with groves of the native lemon tree; a few of which were still sufficiently in fruit to afford us some refreshment.

On the night of December 14-15, when in the same country, only a few miles away, cold weather was encountered, of which Leichhardt wrote (1847, p. 75):

The night was extremely cold, notwithstanding we were encamped under the shelter of trees: and it was therefore evident that we were at a considerable elevation above the level of the sea.

The next account of this species is by Lieut. Col. Mitchell (1848, pp. 188, 209, 221, 231, 353, 434, and maps). This plant was discovered on October 17, 1846, not far from his camp, No. 32, near the juncture of the Maranoa and Merevale Rivers, in the southern part of Queensland, latitude $26^{\circ} S.$ ¹ The drouthy character of the climate is evident from Mitchell's remark (1848, p. 353) that:

We had this day passed over a fine open forest country, in which were also groves of the *Acacia pendula*. The vegetation, in general, seemed drooping, from the want of rain; but the whole was available for grazing purposes.

Among the interesting plants collected was the one in question, of which Mitchell (1848, p. 353) wrote:

A small fruit, with the fragrance of an orange, proved to be a new species of *Triphasia*.†

†*T. glauca* (Lindl. MS.): spinosa, foliis coriaceis integerrimis crenatisque linearibus glaucis obtusis retusisque, floribus trimeris dodecandris 2-3nis brevi-pedicellatis.

The footnote inserted at this point is the original botanical description of the plant.

This plant was found on the return trip to the south, but the expedition had passed through this same region on the way north during June and July (midwinter in that latitude), and the observations made at that time showed the climate to be decidedly cold for a country so near the Tropics. On June 24 Col. Mitchell stated that "the hoar frost had stiffened the grass and the water was frozen so that the horses cared not to drink." The temperature was $17^{\circ} F.$ at 4 a. m. and $21^{\circ} F.$ at sunrise. At this date his party was in the vicinity of Mount Owen, only about 45 miles north-northwest of camp No. 32. On July 2, at camp No. 41, in the valley of the Warrego River (latitude $25^{\circ} S.$, longitude $147^{\circ} 30'' E.$)

¹ This locality is not far from the present village of Forestvale in Dublin County.

the thermometer registered as low as 7° F. at 3 o'clock in the morning and at sunrise 14° F. This was at a point 70 miles north-northwest from the region where the desert kumquat was originally found, but at 1,800 feet altitude instead of 1,300. On July 12, at his camp No. 48, at a point about 100 miles northwest of the locality where *Eremocitrus glauca* was discovered, Mitchell states that the temperature at sunrise was 11° F. This was latitude 24° 50' S.

On June 3 while in the vicinity of Kings Ferry,¹ some 15 miles south of camp No. 32, the type locality of the species, the temperature registered 16° F. at sunrise, which would indicate a possible minimum temperature of about 8° to 10° F., if the same values hold here as at camp No. 41. This was at an altitude of 1,400 feet, nearly the same as at camp No. 32.

It would not be surprising, in view of these scanty records taken at random, if temperatures as low as 5° F., or even zero Fahrenheit, would be found to occur occasionally in the region where the desert kumquat grows wild. Such low temperatures might injure the leaves and perhaps the smaller twigs, but recovery would probably be rapid and complete. Certainly no other edible citrous fruit is native to any region where it is exposed to such severe cold weather.

DROUGHT-RESISTANT ADAPTATIONS OF THE DESERT KUMQUAT

The very first glance at a specimen of *Eremocitrus glauca* shows that it is a pronounced desert plant. * Any one accustomed to seeing desert plants will be struck by the familiar gray-green color of the scanty foliage of small, thick, leathery leaves. So marked is the xerophytic character of the Australian desert kumquat that an experienced botanist on first seeing it exclaimed, "It must be some kind of sagebrush!"

The cuticle is very thick, and the breathing pores are sunk below the surface and have very small air spaces below them. The leaves differ markedly from those of the ordinary citrous fruits in being provided with stomates and palisade tissue on both faces (fig. 5), making the upper

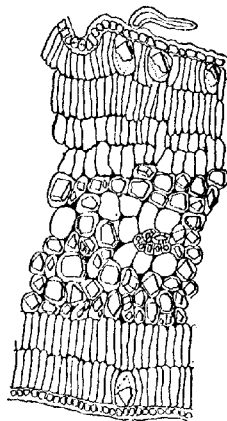


FIG. 5.—*Eremocitrus glauca*: Cross section of leaf from near Forestvale, Queensland, collected by T. L. Mitchell on October 17, 1846; in Gray Herbarium. Shows four ventral and two dorsal strata of palisade cells, central thin-walled cells often containing crystals of calcium oxalate. The outer wall of the epidermis is very thick. A stomate and an appressed hair are shown on the upper surface; these organs occur also on the lower surface. $\times 240$. Drawn by Theodor Holm.

¹ This was near the present town of Donnybrook in Dublin County, Maranoa District.

and lower surfaces very similar in appearance and function; a not uncommon characteristic of desert plants. The leaves are very thick, perhaps because of their double equipment of palisade tissue. The young leaves have a scattered covering of minute short, thick appressed hairs, with a warty cuticle.



FIG. 6.—*Eremocitrus glauca*: A hair from the leaf of a plant grown from seed from near Chinchilla, Queensland (S. P. I. No. 29660). Shows abrupt bend near the base and the cuticular prominences. Such hairs are usually 2- to 4-septate. $\times 372$. Drawn by Theodor Holm.

They bend abruptly at right angles near the base and are from 80 to 135 μ long and 10 to 16 μ wide, often unicellular when young, but usually 2- to 4-septate when old. The wall is thickened internally at the base where it is bent, and the cuticle shows numerous wartlike, oval prominences (fig. 6). These hairs often disappear almost entirely from old leaves. Exactly similar hairs occur on the young twigs. No such persistent coating of hairs occurs on the leaves of any other citrus fruit. It is probable that a study of this plant in the field will show that this coating of this plant in the field will show that this coating

of peculiar hairs serves as a protection to the young twigs and leaves as they are developing.

The young twigs of the Australian desert kumquat are very slender in comparison with those of other citrus trees and are, like the leaves, of a gray-green color. A cross section of a young twig shows the presence of a very thick cuticle and small deeply sunken stomates nearly destitute of air spaces (fig. 7). Both of these characters indicate strongly marked drouth-resistant adaptation. The twigs have below the epidermis a double layer of palisade cells filled with chlorophyll (see fig. 7) and are as well adapted to manufacture starchy food as are the leaves themselves.

Here, again, we find a character common in desert plants, which often drop their leaves in time of severe drouth and utilize their green twigs for as much photosynthesis as the scanty water supply will permit.

That this species must endure severe drouth in its Australian habitat is confirmed by the fact that on the day the type specimens were collected Mitchell observed the wilting of some of the Australian acacias, themselves drouth-resistant plants. A study of the anatomy of the desert kumquat confirms abundantly the natural inference that any

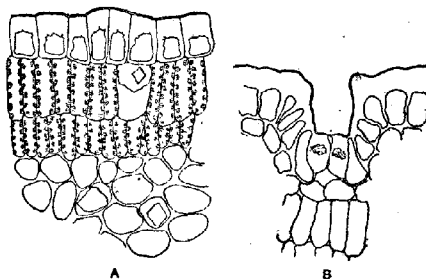


FIG. 7.—*Eremocitrus glauca*: Cross section of the epidermal region of a 1-year-old twig from near Forestvale, Queensland, collected by T. L. Mitchell on October 17, 1946; Gray Herbarium. $\times 248$. A, thick-walled epidermis, two strata of palisade cells, and inner cortical parenchyma; B, a stomate at the bottom of a deep narrow pit. Drawn by Theodor Holm.

citrous fruit to thrive in such conditions must possess marked adaptations to enable it to resist severe drouth.

It is very probable that the ability of this plant to grow in dry soils exposed to hot, dry winds will render it of great value in breeding new types of citrous fruits better fitted than any we now possess to grow under semiarid conditions.

USES OF THE FRUITS OF THE DESERT KUMQUAT

The early explorers of the deserts of southern Queensland and northern New South Wales note repeatedly the fact that the fruits of the desert kumquat are edible.

Leichhardt (1847, p. 77), writing on December 16, 1844, said:

Yesterday in coming through the scrub, we had collected a large quantity of ripe native lemons, . . . we made them into a dish very like gooseberry-fool; they had a very pleasant acid taste, and were very refreshing. They are of a light yellow colour, nearly round, and about half an inch in diameter; the volatile oil of the rind was not at all disagreeable.

At this time Leichhardt was in the region to the west of the Expedition Range at about latitude $24^{\circ} 45' S.$, in what is now Denison County.

About 10 years later Ferdinand von Müller accompanied the North Australian Expedition, under the command of A. C. Gregory, and in his report (1858, p. 143) noted that this species is one of the plants characteristic of the Brigalow Scrub. He called the fruit "a small jemon" and stated that it was among the native fruits eaten by the exploring party.

Prof. J. H. Maiden (1888, p. 489; 1889, p. 8), Colonial Botanist of New South Wales, Australia, said of this species:

'Native Kumquat,' 'Desert Lemon.'

The fruit is globular, and about half-an-inch in diameter. It produces an agreeable beverage from its acid juice. A fair preserve may be made out of the fruit.

Prof. F. M. Bailey (1895, p. 17) wrote as follows:

Atalantia glauca, J. D. Hook. The Kumquat or Lime of our Downs country. Order Rutaceæ, and closely allied to the orange; often attains the size of a small tree, but while only the size of a small shrub yields a great abundance of fruit, which is gathered and converted into jam by the settlers. By careful selection and cross-fertilization from this might be obtained varieties worthy of cultivation for the sake of their fruit.

It is evident from this testimony that the Australian desert kumquat when growing in a wild state yields fruits which, though small, are eaten and even prized by the settlers.

This is also shown by the following account, from a letter of F. S. Carne, dated Fairfield, Roma, Queensland, February 15, 1914, addressed to W. M. Carne, of Sydney, Australia, and by him sent to the author.

* * * The limes flower in the early spring and the fruit is ripe about the end of November. They are to be found principally on broken Brigalow plains in chocolate

soil, mostly shallow and often stony, and seem to have a tendency to form small scrubs covering an acre or so, but in such cases do not bear much fruit. The trees that are growing in small clumps with a fair amount of room between them fruit very heavily and every season. I don't think they bear till at least 5 years old. The trees when mature average about 10 or 12 feet in height and the stem about 6 in. in diameter and about 6 feet from the ground to the limbs. The young trees are very thorny and have very few leaves, but the grown trees are nice and bushy with scarcely any thorns. At certain times of the year they exude a gum of which some people are very fond. It has a slightly tart taste. Although all the grown trees appear of the same kind to me, odd ones have a fruit much larger and the shape of a Lisbon lemon, the fruit of the majority, however, is the shape of the Mandarin. * * * I am sending a bottle of lime jam. We make it every year. * * * Some folk also make pickles of them, and the children use a lot of them for drinks.

(The jam is of the bitter marmalade character and in my opinion a very pleasant novelty. W. M. C[arne].)

Doubtless if this tree were cultivated, fertilized, and irrigated in accordance with the best methods of modern citriculture, fruits of a larger size and of better flavor could be obtained.

It is to be hoped that the botanists and horticulturists of Australia will give more attention to this remarkable species, one of the most interesting of their citrous fruits. This should result in bringing to light unusually hardy, drouth-resistant, large-fruited or otherwise interesting forms.

Even in its present form the Australian desert kumquat is well worthy of culture in regions slightly too dry or too cold to permit ordinary citrous fruits to succeed.

INTRODUCTION OF EREMOCITRUS GLAUCA IN THE UNITED STATES

Through the cooperation of the Office of Foreign Seed and Plant Introduction, seeds of *Eremocitrus glauca* were secured from Queensland, Australia, in April, 1911. On germination the seedlings showed hypogeous cotyledons, succeeded by very slender cataphylls.¹ Very soon long, slender spines were produced near the axil of each leaf. In spite of every effort to force these young seedlings into a vigorous growth, it has proved impossible in the three years that have elapsed to induce the formation of any full-sized leaves such as are seen on specimens collected in Australia. These plants continue to produce cataphylls and very long, slender spines. Even in Australia the trees when young are very thorny and have only very narrow leaves.

Plants have been sent to a number of localities in Florida, Alabama, Louisiana, Texas, New Mexico, Arizona, California, and Oregon for trial and within a year or two it will be possible to ascertain with a fair degree

¹ The Australian species of *Citrus*, *C. australis*, *C. australasica*, and *C. Garrawayi*, germinate in the same way, producing alternate cataphylls which gradually become larger and usually after a few months are replaced by true leaves of nearly full size. These three Australian species of *Citrus*, together with the broad-leaved *C. inodora* F. M. Bail, constitute a very distinct group of species differing from the other species of *Citrus* in a number of other characters, such as the small flowers, with free stamens and a few-celled ovary with only four or six ovules in a cell.

of accuracy the soil and climatic factors which limit the culture of the desert kumquat in the United States.

THE UTILIZATION OF EREMOCITRUS IN BREEDING

From the taxonomic study of *Eremocitrus*, it is clear that its nearest relationship is with the peculiar Australian species of *Citrus* (especially *C. australis* and *C. australasica*), with which it shows close similarities in many characters of fundamental importance, such as the flower and fruit structure and the method of germination.

This close relationship, deduced from the botanical characters, is confirmed by the fact that *Eremocitrus glauca* grows vigorously when grafted on *Citrus australasica* (Pl. VIII, fig. 1) and that *Citrus australasica* grafts readily on *Eremocitrus glauca*. It has been found that *Citrus australasica* hybridizes freely with at least two cultivated species of *Citrus*,¹ and it is not only almost certain that *Eremocitrus glauca* will cross with *Citrus australasica* and the other Australian species of *Citrus*, but also very probable that it will hybridize with the commonly cultivated Asiatic species of *Citrus*.

The desert kumquat, native to the semiarid Australian scrubs, able to withstand severe cold in winter as well as burning heat and extreme dryness both of the soil and air in summer, is the most promising species known for use in breeding new types of hardy citrus fruits. Every effort is being made to hasten its flowering, so that hybrids can be made, using it as one of the parents. The fact that the desert kumquat has edible fruits without any disagreeable acrid oil in the peel or in the juice makes it far more promising than the Chinese trifoliate orange, *Poncirus trifoliata* (L.) Raf. (= *Citrus trifoliata* L.), for breeding hardy citrus fruits for table use.

The discovery of this markedly drouth-resistant species in the Australian scrubs opens the way to the breeding of a new class of citrus fruits, able to grow with much less water than is required by ordinary oranges, lemons, or grapefruits.

GRAFTING AND BUDDING EREMOCITRUS

The Australian desert kumquat can be readily grafted or budded on all of the commonly cultivated species of *Citrus*, such as the orange, grapefruit, lemon, etc., and also on the Australian finger lime (*C. australasica*). It grows very well on the tabog of the Philippine Islands (*Chaetosperrum glutinosa* (Blanco) Swing.), and on the wood-apple of India (*Feronia elephantum* Corr.). (See Pl. VIII.)

The various species of *Citrus* graft easily on *Eremocitrus*, which makes it possible to test this new hardy stock for types of soil to which

¹ Mr. George W. Oliver crossed *Citrus australasica* with *C. mitis* in 1909, and the writer crossed the same species with *C. aurantifolia*, the common lime, in 1913, in the greenhouses of the Department of Agriculture at Washington, D. C. Vigorous hybrids were secured from both of these crosses.

the commonly used citrous stocks are not well adapted. It is not impossible that the desert kumquat, being adapted to grow in desert soils, which are usually more or less saline, will prove able to withstand more "alkali" in the soil than the Asiatic species of Citrus, which are indeed very sensitive to salty soils or water.

Being different from Citrus in so many visible characters, it is possible that Eremocitrus will also differ physiologically and prove resistant to some of the many fungous diseases that attack citrous stocks.

NEED FOR TAXONOMIC STUDY OF THE WILD RELATIVES OF CULTIVATED PLANTS

The bringing to light of the true relationships and possible uses of Eremocitrus, which, although described 66 years ago, has remained to this day practically unknown to botanists and horticulturists, is another link in the chain of arguments going to prove that a better knowledge of the wild relatives of our crop plants is indispensable as a preparation for their improvement by breeding.

It is certainly surprising that a plant so remarkable as *Eremocitrus glauca*, closely related to our cultivated citrous fruits and bearing edible fruits in a wild state, the only desert plant known in the whole orange subfamily, and the hardiest of all the evergreen species, has never before been introduced into culture or utilized in breeding experiments.

Probably the neglect of this remarkably interesting plant in the past has been due largely to the unfortunate nomenclatorial history of the species. Originally placed in *Triphasia*, it would naturally be supposed to be similar to *Triphasia trifolia* (Burm.) Wilson, common in gardens in tropical and subtropical countries. This plant is a small shrub with trifoliate, almost stalkless, leaves, subtended by paired spines. The fruit is a little berry filled with a sweetish and aromatic mucilaginous pulp, very unlike an orange and not at all closely related to the genus Citrus.

After being classed as a species of *Triphasia* for 15 years, the Australian desert kumquat was removed to the genus *Atalantia* by Bentham in 1863. It is true that this placed it in a genus more closely allied to Citrus than is *Triphasia*, but about this time Baillon's view that Citrus is closely related to the Bael fruit (*Aegle marmelos* (L.) Corrêa) and the wood-apple of India began to be accepted generally by botanists, and as a result the possibility of a species of *Atalantia* being closely allied to Citrus seems not to have occurred to any of the botanists who have published concerning this group of plants during the past third of a century.

That the discovery of Eremocitrus is not a unique result of some extraordinary good fortune is shown by the fact that an equally striking and equally misunderstood new genus, *Citropsis* (Swingle and Keller-

man, 1914), also closely related to *Citrus*, has lately been described from tropical Africa and also by the recent discovery of a new and curious species of *Citrus* (Swingle, 1913), growing wild at higher altitudes and farther north than any other previously known species of the genus.

The citrus fruits are perhaps the most interesting and in many ways the best known of all our fruits, so that the surprising lack of knowledge as to the wild relatives of *Citrus* is doubtless duplicated in the case of many other commonly cultivated plants. Until these neglected botanical resources are brought to light and rendered available to the experimenter by critical taxonomic study it is not possible to undertake the improvement of our crop plants in the most rational and effective way. This hybridizing of our crop plants with their wild relatives is a work of the greatest moment at the present time, when the constantly increasing cost of food directs attention to the necessity of extending agriculture by bringing under culture lands too dry, too wet, too salty, too poor, or situated in climates too hot, too cold, or too variable for the culture of the crop plants as they now exist.

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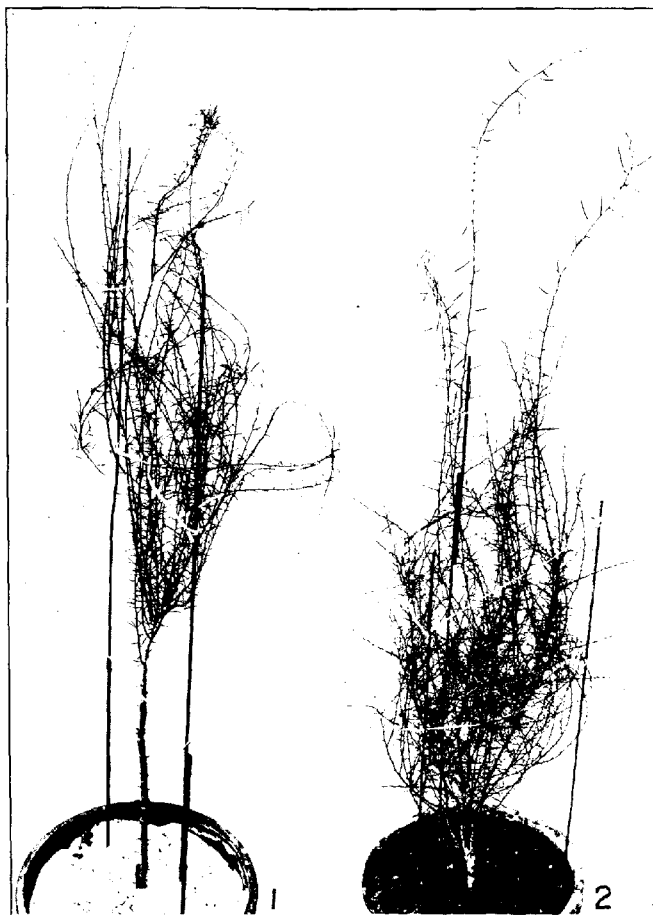
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PLATE VIII

Eremocitrus glauca (Lindl.) Swing. S. P. I. No. 29660. Grown from seed from the Condamine River near Chinchilla, Queensland, Australia. One-eighth natural size.

Fig. 1.—Desert kumquat grafted on the Australian finger lime (*Citrus australasica*).

Fig. 2.—Desert kumquat grafted on the wood-apple (*Feronia elephantum*). Two years' growth.



RELATION OF BACTERIAL TRANSFORMATIONS OF SOIL NITROGEN TO NUTRITION OF CITROUS PLANTS

By KARL F. KELLERMAN, *Physiologist in Charge*, and R. C. WRIGHT, *Scientific Assistant*,
Soil-Bacteriology and Plant-Nutrition Investigations, Bureau of Plant Industry

It is practically certain that there are a number of immediate causes for the decrease in the yield of fruit and for the general physiological decadence of citrus trees apparent in small areas scattered throughout the orange belt in California. In this region, as in many irrigated orchard districts of both deciduous and citrus trees, a high yield of fruit is correlated with a very luxuriant and vigorous vegetative growth of the individual trees. To an observer accustomed to the orchards of the humid regions of the East, this simultaneous enhancement of both the reproductive and vegetative functions of the plant suggests an abnormality due to a general physiological stimulation slightly in excess of the optimum caused by high temperature, excessive insolation, extreme fluctuations in quantity of soil moisture, and an abundant, though perhaps erratic, supply of soil nutrients. Under such conditions a very slight additional stimulus might cause rapid deterioration or injury. While this premise is not essential to the establishment of a relation between changes in soil nitrogen and abnormal nutrition, to recognize this unusual parallel of functions as signalling distinct overstimulation gives a logical reason for expecting similar or identical symptoms of malnutrition in different citrus groves, even though the immediate causes of their decadence within different limited areas might differ widely.

Extensive bacteriological studies upon soils near Riverside, Cal., and occasional examinations of soils of other irrigated regions, together with observations upon the physiology of citrus trees and physiological experiments upon citrus seedlings, are believed to offer defensible hypotheses for advising the employment of certain methods of crop culture to ameliorate at least a portion of the baffling trouble in southern California generally known as citrus malnutrition, chlorosis, or mottle leaf (Smith and Smith, 1911).¹

A careful examination of the soluble-salt content² of soil samples taken throughout southern California showed in common with other investigators (Hilgard, 1906b; Swingle, 1904; Loughridge, 1903, 1911;

¹ Bibliographic citations in parentheses refer to "Literature cited," p. 113.

² Except for the estimation of nitrates, determinations were made in accordance with the methods described by Schreiner, O., and Failyer, G. H., *Colorimetric, turbidity, and titration methods used in soil investigations*, U. S. Dept. of Agr., Bur. Soils Bul. 31. Nitrates were determined by a modification of the Thieman-Schultze method, for explanation of which see Kellerman, K. F., and Smith, N. R., *The absence of nitrate formation in cultures of Azotobacter*, *Cent. f. Bakt. [etc.]*, Abt. 2, Bd. 40, No. 19/21, p. 479-482.

Means and Holmes, 1902, p. 601) a wide variation in the percentage of carbonates, chlorides, nitrates, and sulphates, chiefly of sodium, potassium, calcium, and magnesium, which are the salts usually present in appreciable quantities. From a casual examination of these data there appears to be no relation between soils of high salt content and malnutrition of trees. In figures 1, 2, and 3, however, it is evident that when adjacent areas are compared, the soils from the vicinity of deteriorating trees are richer in nitrate nitrogen. The quantities of other salts show no constant relationship to good or poor areas. Except for a slight increase in the quantity of bicarbonates during the spring, there is no evidence of seasonal

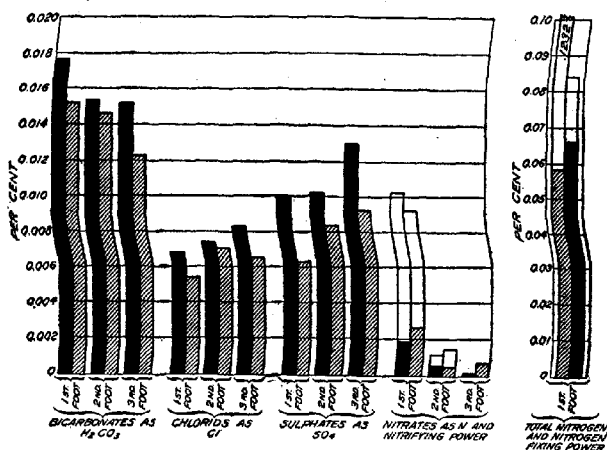


FIG. 1.—Diagram showing relative nitrogen-fixing power, nitrifying power, and salt content of soil samples from good and poor areas in an orange grove which was unproductive and markedly chlorotic throughout. The good areas were themselves very unproductive.¹ Black columns show good areas; hatched columns indicate poor areas.

variation for the various salts. Though decided variations in salt content of the soil were observed occasionally, they were evidently due to the infrequent rains.

The nitrate content of the soil of so-called "poor" areas is not excessive unless the crust analyses shown in figure 4 are taken into account. During irrigation it is obvious that in the poor areas the numerous shallow lateral roots (Mills, 1902) will be bathed in a solution which temporarily is relatively stronger than during the intermediate periods. The reports that in some cases applications of fertilizers high in nitrogen to orange groves showing symptoms of malnutrition have accelerated instead of retarded the deterioration offer corroborative evidence of the danger of an excessive supply of readily available nitrogen. It is, of

¹ The samples were collected near Riverside, Cal., in June, July, August, and October, 1912, and February, March, and June, 1913. The averages of the analyses are given.

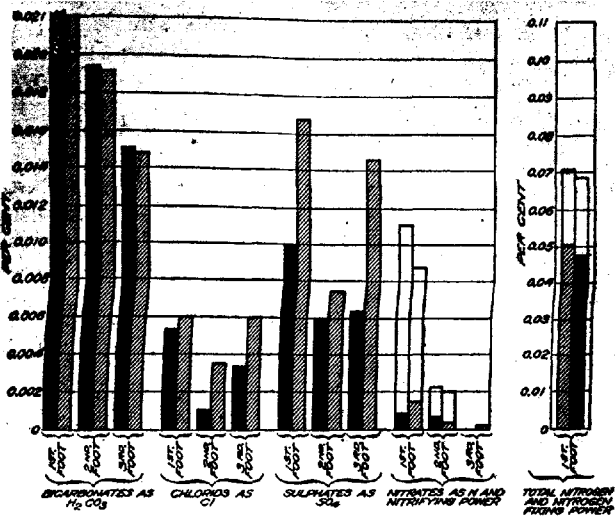


FIG. 2.—Diagram showing relative nitrogen-fixing power, nitrifying power, and salt content of good and poor areas in an orange grove that produced a fair crop of marketable fruit. The poor areas were unproductive.¹ Black columns show good areas; hatched columns indicate poor areas.

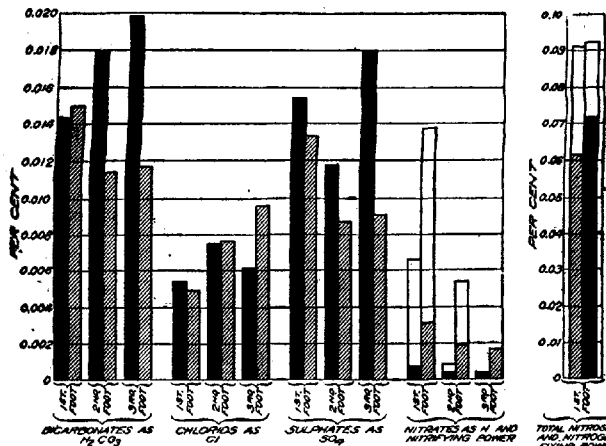


FIG. 3.—Diagram showing relative nitrogen-fixing power, nitrifying power, and salt content of soil samples from good and poor areas in an orange grove which showed decided symptoms of chlorosis associated with small yields of low-grade fruit. There was but a slight difference in the vigor of the orange trees² growing upon the good and the poor areas.³ Black columns show good areas; hatched columns indicate poor areas.

¹ The samples were collected near Riverside, Cal., in June, July, August, and October, 1912, and February, March, and June, 1913. The averages of the analyses are given.

² The trees of this grove were considered as probably unusually sensitive, because the stock, originally budded to lemons, was later budded to oranges, thus leaving a portion of the lemon trunk in the trees.

³ The samples were collected near Riverside, Cal., in October, 1912, and February, March, and June, 1913. The averages of the analyses are given.

course, recognized that records of fertilizer practice in California are meager and unsatisfactory. Somewhat extensive greenhouse experiments have been carried on in Washington, and although laboratory results can not be directly translated into field conditions, the results

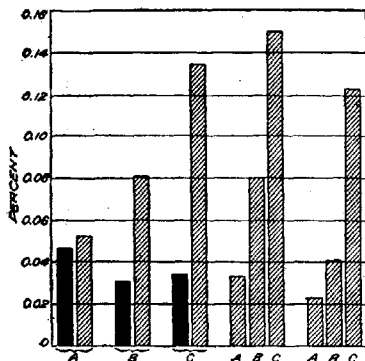


FIG. 4.—Diagram showing quantities of salts found in crust samples of soil from the same areas illustrated in figures 1, 2, and 3.

again indicate that nitrate nitrogen in excess produces the typical symptoms of malnutrition. In the experiments reported in detail in Tables I, II, and III both greenhouse soil and virgin California soil from typical orange-growing areas were used. Moderate quantities of nitrate gave no apparent result, but it has been noted in earlier publications (Moore and Kellerman, 1905) that toxic limits established in the laboratory may be expected to be much higher

than will be found to exist under a natural and favorable environment. If the hypothesis of overstimulation in southern California is accepted, a wide variation between the low inhibiting or toxic limits in the field and comparatively high toxic limits found in the greenhouse in Washington is therefore to be expected.

TABLE I.—Effect of certain salts and combinations of salts on grapefruit seedlings growing in greenhouse soil at the Department of Agriculture, Washington, D. C.^a

Lab- oratory No.	Soil treatment.	Condition of trees after 74 days.	Condition of trees after 144 days.
770	Check	Normal	Normal.
771	do.	do.	Do.
772	CaCO ₃ (5 per cent)	do.	Slight leaf burning (?)
773	do.	do.	Normal.
774	N as KNO ₃ (0.04 per cent)	Leaves shed.	Leaves shed.
775	do.	Leaves burning.	Leaves burning.
776	CaCO ₃ (1 per cent) + N as KNO ₃ (0.04 per cent)	Leaves shed.	New leaves; chlorotic.
777	do.	do.	Do.
778	Cl as NaCl (0.04 per cent)	Normal	Leaves burning.
779	do.	do.	Do.

^a Grapefruit seedlings 2 years and 4 months old, about 24 inches in height, were transplanted into 6-inch pots of soil mixture consisting of equal parts of sand and soil composted in rather stiff clay soil.

TABLE I.—Effect of certain salts and combinations of salts on grapefruit seedlings growing in greenhouse soil at the Department of Agriculture, Washington, D. C.—Con.

Lab- oratory No.	Soil treatment.	Condition of trees after 74 days.	Condition of trees after 144 days.
780	Cl as NaCl (0.04 per cent) + N as KNO ₃ (0.04 per cent).	Leaves shed.....	Few new leaves; chlorotic.
781do.....do.....	Do.
782	CaCO ₃ (1 per cent) + Cl as NaCl (0.04 per cent).	Normal.....	Normal.
783do.....do.....	Do.
784	HCO as NaHCO ₃ (0.04 per cent).do.....	Do.
785do.....do.....	Do.
786	HCO as NaHCO ₃ (0.04 per cent) + N as KNO ₃ (0.04 per cent).	Leaves shed.....	Do.
787do.....do.....	New leaves normal.
788	SO ₄ as Na ₂ SO ₄ (0.04 per cent) + N as KNO ₃ (0.04 per cent).	Normal.....	Leaves nearly all shed.
789do.....do.....	Do.

TABLE II.—Effect of certain salts and combinations of salts on sour-orange seedlings growing in California soil at Washington, D. C.^a

Lab- oratory No.	Soil treatment.	Condition of trees after 26 days.	Condition of trees after 46 days.	Condition of trees after 90 days.
930	Check.....	Normal.....	Normal.....	Normal; growing.
931do.....do.....do.....	Do.
932	CaCO ₃ (1 per cent).....do.....do.....	Do.
933do.....do.....do.....	Do.
934	CaCO ₃ (3 per cent).....do.....do.....	Do.
935do.....do.....do.....	Do.
936	CaCO ₃ (10 per cent).....do.....do.....	Do.
937do.....do.....do.....	Do.
938	N as KNO ₃ (0.02 per cent) ^bdo.....do.....	Do.
939do. ^cdo.....do.....	Do.
940	N as KNO ₃ (0.04 per cent) ^d	Dead; replanted.	Dead.....	Dead.
941do. ^e	Normal.....	Normal.....	Subnormal.
942	N as KNO ₃ (0.06 per cent) ^f	Dead; replanted.	Dead.....	Dead.
943do. ^gdo.....do.....	Do.
944	Cl as KCl (0.02 per cent).....	Normal.....	Normal.....	Subnormal.
945do.....do.....do.....	Normal; growing.

^a Sour-orange seedlings 48 days old were transplanted into 4-inch paraffined pots containing virgin soil taken from near Riverside, Cal. Plants were watered with distilled water. All drainage water was caught and returned to each pot, thus preventing any change in salt content.

Percentage of nitrates present after 90 days: ^b 0.0018 per cent. ^c 0.0061 per cent. ^d 0.0213 per cent. ^e 0.0087 per cent. ^f 0.0200 per cent. ^g 0.0194 per cent.

TABLE II.—Effect of certain salts and combinations of salts on sour-orange seedlings growing in California soil at Washington, D. C.—Continued.

Laboratory No.	Soil treatment.	Condition of trees after 26 days.	Condition of trees after 46 days.	Condition of trees after 90 days.
946	Cl as KCl (0.05 per cent).....	Dead; replanted.	Dead.....	Dead.
947	do.....	Normal.	Subnormal.	Do.
948	Cl as KCl (10 per cent).....	Dead; replanted.	Dead.....	Do.
949	do.....	Normal.	do.....	Do.
950	N as KNO ₃ (0.04 per cent) + CaCO ₃ (1 per cent). ^k	do.....	Burning.....	Subnormal.
951	do. ^l	Dead; replanted.	Normal.....	Do.
952	N as KNO ₃ (0.04 per cent) + CaCO ₃ (3 per cent). ^j	do.....	Burning.....	Normal; growing.
953	do. ^k	Normal.....	Dead.....	Dead.
954	N as KNO ₃ (0.04 per cent) + CaCO ₃ (10 per cent). ^l	Dead; replanted.	Normal.....	Normal; growing.
955	do.....	Normal.....	do.....	Subnormal.
956	N as KNO ₃ (0.04 per cent) + Cl as KCl (0.05 per cent).	do.....	Dead.....	Dead.
957	do.....	do.....	Burning.....	Do.
958	N as KNO ₃ (0.04 per cent) + Cl as KCl (0.05 per cent). ^o	do.....	Dead.....	Do.
959	do. ^p	do.....	do.....	Do.
960	N as KNO ₃ (0.02 per cent) + Cl as KCl (0.02 per cent). ^m	Dead; replanted.	do.....	Normal; growing.
961	do. ⁿ	do.....	do.....	Do.
962	Cl as KCl (0.05 per cent) + CaCO ₃ (3 per cent).	do.....	do.....	Do.
963	do.....	do.....	do.....	Do.
964	Cl as KCl (0.05 per cent) + CaCO ₃ (10 per cent).	do.....	do.....	Subnormal.
965	do.....	do.....	do.....	Do.
966	Cl as KCl (0.02 per cent) + CaCO ₃ (3 per cent).	Normal.....	Normal.....	Normal; growing.
967	do.....	do.....	do.....	Do.

Percentage of nitrates present after 90 days: ^k 0.0095 per cent. ^l 0.0035 per cent. ^j 0.0046 per cent. ^k 0.0238 per cent. ^l 0.00485 per cent. ^m 0.0012 per cent. ⁿ 0.0017 per cent. ^o 0.0081 per cent. ^p 0.0130 per cent.

TABLE III.—Effect of certain salts and combinations of salts on grapefruit seedlings growing in California soil at Washington, D. C.^a

Lab- oratory No.	Soil treatment.	Condition of trees after 22 days.	Condition of trees after 48 days.	Condition of trees after 88 days.
892	Check.....	Normal.....	Normal.....	Normal; growing.
893	do.....	do.....	do.....	Do.
894	CaCO ₃ (1 per cent).....	do.....	do.....	Do.
895	do.....	do.....	do.....	Do.
896	CaCO ₃ (3 per cent).....	do.....	do.....	Do.
897	do.....	do.....	do.....	Do.
898	CaCO ₃ (10 per cent).....	do.....	do.....	Do.
899	do.....	do.....	do.....	Do.
900	N as KNO ₃ (0.03 per cent) ^b	do.....	do.....	Do.
901	do. ^c	do.....	do.....	Do.
902	N as KNO ₃ (0.04 per cent) ^d	Dead; replanted..	Dead.....	Dead.
903	do. ^e	do.....	Normal.....	Do.
904	N as KNO ₃ (0.06 per cent) ^f	Normal.....	Dead.....	Do.
905	do. ^g	Dead; replanted..	do.....	Do.
906	Cl as KCl (0.02 per cent).....	Normal.....	Normal.....	Normal; growing.
907	do.....	do.....	do.....	Do.
908	Cl as KCl (0.05 per cent).....	do.....	Dead.....	Dead.
909	do.....	Dead; replanted..	do.....	Do.
910	Cl as KCl (10 per cent).....	Normal.....	do.....	Do.
911	do.....	do.....	do.....	Do.
912	N as KNO ₃ (0.04 per cent) + CaCO ₃ (1 per cent) ^h	Dead; replanted..	do.....	Do.
913	do. ⁱ	Normal.....	do.....	Do.
914	N as KNO ₃ (0.04 per cent) + CaCO ₃ (3 per cent) ^j	do.....	do.....	Do.
915	do. ^k	do.....	do.....	Do.
918	N as KNO ₃ (0.04 per cent) + CaCO ₃ (10 per cent) ^l	Dead; replanted..	Subnormal.....	Normal; growing.
919	do. ^m	do.....	do.....	Do.
924	N as KNO ₃ (0.03 per cent) + Cl as KCl (0.02 per cent) ⁿ	Normal.....	Dead.....	Dead.
925	do. ^o	do.....	do.....	Do.
920	N as KNO ₃ (0.04 per cent) + Cl as KCl (0.02 per cent) ^p	Dead; replanted..	do.....	Do.
921	do. ^q	do.....	Normal.....	Subnormal.

^a Grapefruit seedlings 3 months old were transplanted into paraffined pots containing virgin soil taken near Riverside, Cal. Plants were watered with distilled water. All drainage water was caught and returned to each pot, thus preventing any change in salt content.

Percentage of nitrates present after 88 days: ^b 0.0019 per cent. ^c 0.0018 per cent. ^d 0.0117 per cent. ^e 0.0041 per cent. ^f 0.0200 per cent. ^g 0.0205 per cent. ^h 0.0223 per cent. ⁱ 0.0270 per cent. ^j 0.0157 per cent. ^k 0.0183 per cent. ^l 0.0039 per cent. ^m 0.0029 per cent. ⁿ 0.0023 per cent. ^o 0.0044 per cent. ^p 0.0213 per cent. ^q 0.0091 per cent.

TABLE III.—Effect of certain salts and combinations of salts on grapefruit seedlings growing in California soil at Washington, D. C.—Continued.

Lab- oratory No.	Soil treatment.	Condition of trees after 22 days.	Condition of trees after 43 days.	Condition of trees after 53 days.
922	N as KNO_3 (0.04 per cent) + Cl as KCl (0.05 per cent).†	Normal.....	Subnormal....	Subnormal.
923	do.†.....	Dead; replanted.	Dead.....	Dead.
926	Cl as KCl (0.02 per cent) + CaCO_3 (3 per cent).	Normal.....	Normal.....	Normal; growing.
927	do.....	do.....	do.....	Subnormal.
926	Cl as KCl (0.05 per cent) + CaCO_3 (3 per cent).	do.....	Dead.....	Dead.
927	do.....	do.....	do.....	Do.
928	Cl as KCl (0.05 per cent) + CaCO_3 (10 per cent).	do.....	Normal.....	Do.
929	do.....	do.....	do.....	Do.

Percentage of nitrates present after 53 days: † 0.0049 per cent. ‡ 0.0275 per cent.

It should be noted also that the virgin California soil used in these experiments would naturally endure greater additions of nitrate salts

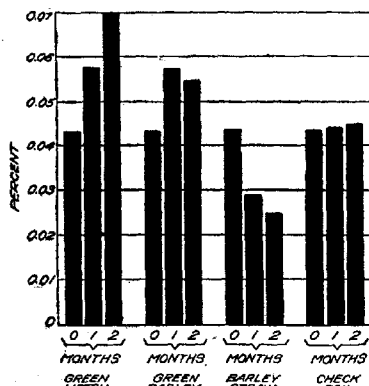


FIG. 5.—Diagram showing effect upon nitrate nitrogen in samples of California soil of additions of 2 per cent of green vetch, green barley, and mature barley straw.

before the toxic limit of orange plants would be reached than would the soils of the older groves. In the latter soils there has been an appreciable accumulation of soluble salts, and, as will be shown later, this would intensify the effect of high nitrates.

As will be seen by an examination of the analyses of nitrate nitrogen made at the close of several experiments, a considerable though rather erratic decrease of this salt took place, and it is probable that this denitrification

occurred during the early periods. The toxic limits of the pot experiments therefore are actually between 0.05 and 0.0100 per cent, as against 0.005 to 0.015 per cent in the field, exclusive of crusts. It is evident, therefore, that nitrates are more fatal than chlorids, that nitrates and chlorids together intensify the symptoms of injury, and that moderate quantities of lime—less than 10 per cent of calcium carbonate

(Hilgard, 1906a)—exert a more or less pronounced protective action. Sulphates are comparatively innocuous and are not reported upon. In this connection it should be noted that while, as would be expected from the analogy of California soils with the soils of the citrous regions of Florida, rather large quantities of calcium carbonate are favorable to the citrous plants, even slight traces of calcium oxid or calcium hydrate have an immediate toxic effect. The beneficial effect of calcium carbonate in flocculating the impervious soils and thus facilitating their permeability to irrigation water renders it valuable from a physical as well as a biological standpoint in many areas.

While no adequate data are recorded, records of at least temporary benefit from the application of nitrate fertilizers to chlorotic orange groves are available. Laboratory and greenhouse studies offer a possible explanation of such a phenomenon under certain conditions. As shown in figures 5, 6, and 7, different substances which are commonly plowed under to maintain humus in the soil show pronounced differences in their effect upon the soil bacteria. Mature barley straw or pure cellulose rapidly reduces the nitrate content of a soil¹ and may eliminate it entirely if it is present in relatively small quantities; furthermore, although but little nitrogen is actually lost, it seriously delays the nitrification into nitrate. Green manures, on the other hand, while causing some actual loss of total nitrogen, do not materially disturb the ratios of the nitrogenous compounds. The same order of limitation is shown by these substances in their effect upon the nitrification of pepton in the soil. As shown in Tables IV and V, seedling citrous plants were actually forced by the addition of cellulose and of straw into an apparently typical state of malnutrition through nitrogen starvation caused by the unbalancing of the soil flora and the utilization of all of the nitrate by the organisms which decompose straw and cellulose.²

¹ From unpublished results in 1911. Any mature straw, as well as pure cellulose, causes a rapid denitrification of soil nitrate, and the subsequent nitrification which again forms nitrate is very slow. (See also Lipman, J. G., and Brown, Percy E., 1909.)

² From unpublished results in 1907, showing injury to corn by the bacterial denitrification of nitrate to nitrite, it was supposed that nitrite poisoning might be the cause of the injury to citrous plants in the conditions shown in Table V. The presence of appreciable quantities of nitrite in the soil supporting apparently normal citrous plants indicates that complete elimination of nitrate is more injurious to them than is the formation of slight quantities of nitrite.

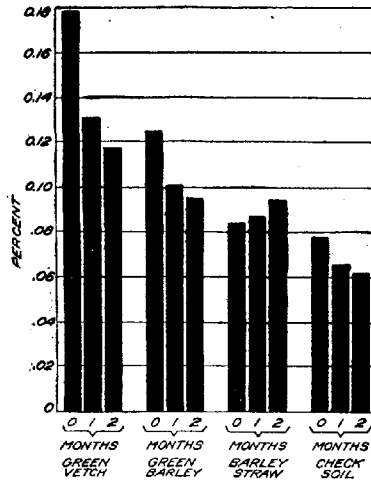


FIG. 6.—Diagram showing effect upon total nitrogen, not including nitrate nitrogen, in samples of California soil of additions of 1 per cent of green vetch, green barley, and mature barley straw.

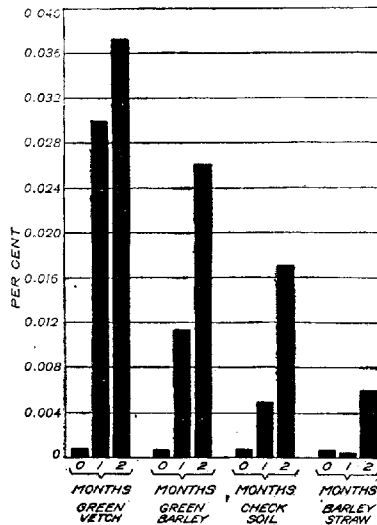


FIG. 7.—Diagram showing effect of additions of 1 per cent of green vetch, green barley, and mature barley straw upon the nitrifying power of samples of California soil.

TABLE IV.—Effect of green manure, straw, pure cellulose, and nitrate on grapefruit seedlings growing in greenhouse soil at the Department of Agriculture, Washington, D. C.^a

Lab- oratory No.	Soil treatment.	Condition of trees after 19 days.	Condition of trees after 57 days.	Condition after 166 days.
734	Check.....	Normal.....	Normal.....	Normal.
735do.....do.....do.....	Do.
736	KNO ₃	Slightly chlorotic.....do.....	
737do.....do.....do.....	
738	Wheat straw (1 per cent).....do.....	Slightly yellowish.....	Yellow and spotted.
739do.....	Normal.....do.....	Do.
740	Wheat straw (1 per cent) + KNO ₃	Chlorotic.....	Normal.....	
741do.....do.....do.....	
742	Green sweet clover (1 per cent).....do.....do.....	Normal.
743do.....do.....do.....	Do.
744	Green sweet clover + KNO ₃	Subnormal.....do.....	
745do.....	Chlorotic.....do.....	
746	Green devil's grass (1 per cent).....	Slightly chlorotic.....do.....	Do.
747do.....do.....do.....	Do.
748	Green devil's grass + KNO ₃do.....do.....	
749do.....	Chlorotic.....do.....	
750	Filter paper (1 per cent).....do.....	Yellow.....	Yellow and spotted.
751do.....do.....do.....	Very yellow and spotted.
752	Filter paper (1 per cent) + KNO ₃	Very chlorotic.....	Normal.....	
753do.....do.....do.....	

^a Grapefruit seedlings about 2½ months old were transplanted into 6-inch pots of greenhouse bench soil.

^bAll organic materials added were cut fine and 1 per cent added dry-weight basis. Nitrogen as nitrate was added once a week to Nos. 735, 737, 740, 741, 744, 745, 747, 749, 752, and 753 at the rate of 0.01 percent at each application. The spotted condition of the leaves where straw and filter paper were used seems to be a symptom of malnutrition in an advanced stage. These leaves showed no "veining" after the first few days.

TABLE V.—Effect of straw and nitrate on sweet-orange, sour-orange, and grapefruit seedlings growing in California soil at Washington, D. C.^aSOUR ORANGE (*Citrus aurantium* L.).

Lab- oratory No.	Soil treatment.	Condition of seedlings after 73 days.
964	Check.....	Normal; growing.
965do.....	Do.
966	Finely ground straw (1 per cent).....	Yellowish.
967do.....	Do.
968	Finely ground straw (2 per cent).....	Do.
969do.....	Do.
970	Finely ground straw (1 per cent) + N as KNO ₃ (0.02 per cent).....	Normal; growing.
971do.....	Do.
972	Finely ground straw (2 per cent) + N as KNO ₃ (0.02 per cent).....	Do.
973do.....	Do.

SWEET ORANGE (*Citrus sinensis* Osb.).

988	Check.....	Normal; growing.
989do.....	Do.
974	Finely ground straw (1 per cent).....	Yellow.
975do.....	Do.
976	Finely ground straw (1 per cent) + N as KNO ₃ (0.02 per cent).....	Normal; growing.
977do.....	Do.

GRAPEFRUIT (*Citrus grandis* Osb.).

986	Check.....	Normal.
987do.....	Do.
978	Finely ground straw (1 per cent).....	Yellow.
979do.....	Do.
980	Finely ground straw (1 per cent) + N as KNO ₃ (0.02 per cent).....	Normal.
981do.....	Do.

^a Orange and grapefruit seedlings about 2 months old were transplanted into paraffined pots containing virgin soil from near Riverside, Cal.; plants were watered with distilled water; all drainage was caught and returned to each pot, thus preventing any change in salt content.

The destruction of cellulose by molds and bacteria is extremely rapid in both good and poor areas, but no correlation of laboratory results and field conditions has as yet been possible. The total number of bacteria in good and poor areas is erratic and seems without significance.

The total nitrogen content and also the nitrogen-fixing power of the poor soils is slightly above that of the good soils, as shown in figures 1, 2, 3, and 4. Similar data have been reported by Headden (1910) for soils of the irrigated orchard regions of Colorado. Contrary to Headden's

opinion, however, this appears to be without significance, as both good and poor soils usually contain rather large quantities of insoluble nitrogen. The control of the rate of nitrification is, on the other hand, of fundamental importance. In pot experiments a normal rate of nitrification is shown to be possible with a green crop turned under, and it seems reasonable to recommend this practice in the field for maintaining the humus supply of the soil. The evidence of the above experiments suggests that the extensive use of mature straw is to be avoided, though light applications of straw to fields too high in nitrate, probably also with the liberal use of ground limestone, might be advantageous.

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AROMA OF HOPS: A STUDY OF THE VOLATILE OIL WITH RELATION TO THE GEOGRAPHICAL SOURCES OF THE HOPS

By FRANK RABAK,

*Chemical Biologist, Drug-Plant and Poisonous-Plant Investigations,
Bureau of Plant Industry*

At the present time the principal method for distinguishing the kind and source of hops is by means of their appearance and odor. This must necessarily be an uncertain and crude method because of the inability of individuals to differentiate accurately between similar odors, and, hence, it can serve only to determine extremes in the quality of the hops. If, therefore, a scientific method based on the actual properties of the hops could be worked out, it would be considerably more satisfactory and accurate. Since the aroma, which is conceded to be an important factor in judging hops, can be readily concentrated in the volatile oil, it was thought that a systematic comparison of the properties of oils distilled from hops obtained from the various hop-producing countries of the world and grown during different seasons would give information which would be valuable not only as a means for judging the quality but also to determine the geographical source of the hops.

FACTORS WHICH INFLUENCE THE AROMA OF HOPS

Since altitude, light, hygrometric conditions, and the composition of the soil affect the composition of the volatile oils of thyme, lavender, rosemary, and peppermint (Jeancard and Satie, 1909; Bonnier, 1894; Lamothe, 1908; Mossler, 1912)¹, it may be easily seen that hops grown in separated localities under different conditions of climate and soil may be widely different in aroma and may produce volatile oils with distinct and constant variations in their chemical properties. This assumption is practically substantiated by Briant and Meacham (1896), who discuss the influence of climate, ripeness, soil, drying, and general manipulation on the value of hops. The amount of rain and sunshine alters the conditions of ripening, and the different degrees of ripeness have a decided effect upon the quality of the hops. Regarding the influence of soil upon the quality of the product, these authors state:

The effect of soil is, however, undoubtedly very great, for it comes within our experience that on two farms in the same neighborhood but with different soils the hops grown upon one are year after year of a decidedly superior character both as regards resins and flavor, to those on the other, although both are farmed in similar manner and with practically the same climatic conditions.

¹ Bibliographic citations in parentheses refer to "Literature cited," p. 158-159.

According to Sykes and Ling (1907), it is well known that hops grown in different parts of the world differ in aroma. It is further stated that, since the oil from California hops yields the same compounds as the oil from Bavarian or English hops, the difference in odor must be due to the different proportions in which the constituents exist.

While it can not be said with certainty that the aromatic constituents of hops are useful industrially, yet they are of sufficient importance not to be overlooked. Concerning the use of the volatile oil in determining the value of hops, Chapman (1898, p. 233) observes:

It is, in the first place, perhaps, the surest guide to the general value of a sample of hops, when reliance is placed upon a physical examination alone * * *. In the selection of hops * * * the essential oil is certainly the constituent to which chief attention should be paid.

Hops with a fine, agreeable bouquet are usually preferred to those with a poorer odor. If, therefore, differences in odor are clearly perceptible in different hops, a comparison of the volatile oils should be most important in determining possible differences in the aromatic quality of the hops. Since the volatile oil is the carrier of the aroma and since the aroma is a factor in judging hops, it should be possible to compare the aroma of one sample of hops with another by means of the volatile oil from each.

ESTERS AS THE PRINCIPAL ODOR BEARERS

Since esters are important factors in determining the odorous quality of volatile oils, it was thought that perhaps this would be a good point of attack for the comparison of the various hop oils. The very agreeable odor of the oil of hops would indicate the presence of esters, and a preliminary test showed them to be present in considerable quantity.

The ester content is easily measured and may be expressed by the ester number. While this value does not express the exact percentage of any particular ester, yet for comparative purposes it answers equally well. For the purpose, therefore, of making a logical chemical comparison of the several oils, the ester value was adopted as being possibly the constant most likely to show any fluctuation which would have a direct bearing on the aromatic quality.

PHYSICAL AND CHEMICAL PROPERTIES OF OILS AS A BASIS FOR COMPARISON

The physical properties of volatile oils often show variations sufficient to enable comparisons to be made. The specific gravity of most volatile oils is an important factor in their investigation and is influenced to a considerable extent by the source and condition of the plant from which the oil is distilled, as well as by the nature of the constituents of the oil. Optical rotation is a property of volatile oils which is very important,

being dependent almost entirely upon the character of the chemical constituents of the oils. Refraction, although less important than either specific gravity or optical rotation, is of value, since some relationship is known to exist between the chemical compounds and their refractive power. Another physical property which is largely affected by the character of the constituents of the oil is its solubility in alcohol or in dilute alcohol. The presence of terpenes in oils retards solubility, while oxygenated compounds, such as esters and alcohols, increase it.

The boiling points of the various constituents differ considerably. This property is often utilized in the examination of oils for the purpose of effecting a partial separation of the constituents by fractional distillation. The thoroughness of this separation depends largely upon the form of the distilling flask and upon the rapidity of distillation.

All these physical properties were determined for the various samples of hop oils in the hope of detecting any possible differences which might exist.

For further comparison, acidity and saponification values were also determined, although they are of less importance. The determination of alcohols, while important in many oils, was not feasible in this investigation because of the nature of hop oil. It was found that acetylation would not take place quantitatively, and, hence, a measurement of the alcohol content was impossible.

An approximate comparison of the terpene and sesquiterpene content was made possible from the fractionation experiments.

Inasmuch as there is no direct method of assay available which is applicable to oil of hops, it was thought that a careful determination of certain physical and chemical properties of different hop oils would yield data from which a logical comparison could be made. All of the above-mentioned physical and chemical constants are likely to vary with the different conditions of climate, soil, cultivation, ripening, and curing of the hops.

GENERAL PLAN OF COMPARISON OF VARIOUS HOPS AND HOP OILS

In order to learn whether any constant differences exist in the various kinds of hops, it was planned to compare the oils distilled from hops grown in the hop-producing sections of the United States with the oil distilled from an authentic sample of imported hops, all the samples to be from hops grown during the same season. The sections chosen in the United States were California, Oregon, Washington, and New York. The imported hops were from Bohemia.

A comparison of oils obtained from the hops during a single season would give results which would be valuable in determining differences for that particular season, but it was of the most importance to ascertain whether the same differences occurred from year to year. Therefore the experiments were carried on for four successive seasons, and

the oils obtained from the hops of any one locality were compared with those from the same locality during these years. This procedure permitted an absolutely fair comparison by which similarities or differences in the properties of the oils could be easily followed and any fluctuations readily noted.

DISTILLATION OF THE VOLATILE OILS

The usual method of steam distillation was applied for the extraction of the volatile oils from the various samples of hops. The conditions of distillation were practically identical in all cases, each sample being distilled until no more oil was noticeable. From 100 to 200 pounds of California, Oregon, and Washington hops and from 50 to 100 pounds of New York and imported hops were distilled. The California hops were from Perkins, Cosumne, Ukiah, and Wheatland. The Oregon samples were from Independence, the Washington samples from Chehalis, and the New York samples from near Waterville. All were representative samples of commercial, sulphured hops. The imported hops were from Saaz, Bohemia. The distilling apparatus consists of a steel body, steel head, condenser, and receiver.^a The material to be distilled was packed firmly in the still, to which the steel head was then securely clamped, after which steam was passed slowly through the material and the condensed vapors collected in the receiver, the volatile oil separating in a distinct layer on the aqueous distillate.

The yields of oil obtained from the various hops during the four successive seasons are given in Table I.

TABLE I.—Yields of volatile oil from various hops during the years 1906 to 1909, inclusive.

Source of hops.	Years.					Average.
	1906 (cold storage).	1906	1907	1908	1909	
California:	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Perkins No. 1.....			0.20	0.38	0.43	0.336
Cosumne.....			.32	.24	.42	.326
Perkins No. 2 ^b37	.33	.350
Ukiah.....			.23	.53	.28	.346
Wheatland.....			.21	.20	.44	.283
Oregon.....	0.30	0.34		.32	.30	.290
New York.....		.32	.16	.14	.15	.192
Washington.....				.36	.38	.370
Imported (Saaz).....	.33	.45	.32	.23	.24	.310

^a A detailed description of the distilling apparatus is given in Bulletin 195 of the Bureau of Plant Industry (Rabak, 1910).

^b Grown at the Brewer ranch, located near Perkins, on the opposite side of the American River.

Considerable variation exists in the yield of oil from the different California hops, not only among the different samples of any one season, but also among the same hops during successive seasons. The average yield of oil from all the California hops during 1907, 1908, and 1909 was 0.32 per cent. Perkins, Cosumne, and Ukiah hops yielded oils which averaged very well during the three seasons. The oil from the Wheatland hops was somewhat below the general average.

The Oregon hops which were distilled during the four successive years showed an average oil content of 0.29 per cent, which is a trifle less than the average California sample.

The New York hops, with an average during the four years of 0.192 per cent of oil, were noticeably lower in oil content than any of the other hops distilled. Only in one year, 1906, did the yield approach that of the California, Oregon, Washington, or the imported hops.

The Washington hops, which were distilled only during two seasons, appear to possess the highest percentage of oil, the average being 0.37 per cent.

The imported hops distilled from the crops of 1906, 1907, 1908, and 1909 showed an average yield of 0.31 per cent of oil, considerable change appearing from season to season.

When distilled for a period of more than two seasons, all the hops showed considerable fluctuation in the yield of oil. Named in the order of their average yield the hops group themselves as follows: Washington, California, imported (Saaz), Oregon, and New York.

This variability in the oil content may be ascribed to varying conditions of climate and soil, as well as to ripeness and drying of the hops, which would affect the formation of the oil in the plant. Slight differences in yield of oil would not necessarily influence the quality, since the same proportion of odoriferous constituents may still be present.

PHYSICAL PROPERTIES OF THE VARIOUS OILS

The physical properties of the oils permit a somewhat better means for comparison, and therefore a record was made of the color, odor, and taste of each of the oils mentioned. Differences in color are, of course, readily noted, but differences in odor and taste are considerably less noticeable, because of the difficulty with which the senses of smell and taste distinguish closely related substances. The specific gravity, refractive power, and solubility, each of which can be accurately measured, are of much greater importance, although even these properties are usually entirely inadequate for detecting constant differences. However, as they are affected by the constituents of the oils they are sometimes of considerable value. In all cases the oils were too dark to permit making determinations of the optical rotation, which is often useful in detecting certain differences in composition. The tabulation shows the physical properties of the various hop oils distilled during the seasons 1907, 1908, and 1909 (Table II).

TABLE II.—Physical properties of various hop oils distilled during several successive seasons.

COLOR.			
Source of hops.	1907 crop.	1908 crop.	1909 crop.
California:			
Perkins No. 1.....	Brownish red.....	Dark brownish red.....	Light brownish red.
Cosumne.....	Light brownish red.....	do.....	Dark brownish red.
Perkins No. 2.....	Pale brown.....	Pale brown.....	Wine red.
Ukiah.....	Dark brownish red.....	Reddish brown.....	Do.
Wheatland.....	Pale brown.....	do.....	Reddish brown.
Oregon.....	Wine red.....	do.....	Dark reddish brown.
New York.....	Deep brownish red.....	Bright brownish red.....	Deep brownish red.
Washington.....	Light brownish red.....	Light brownish red.....	Light wine red.
Imported (Saaz).....	Brown.....	Brownish red.....	Dark brown.
ODOR.			
California:			
Perkins No. 1.....	Strongly aromatic, characteristic.	Strongly aromatic, musty, not agreeable.	Strongly aromatic, not unpleasant.
Cosumne.....	Agreeable, hop-like, very aromatic.	Pleasant, aromatic, hop-like.	Strongly aromatic, agreeable.
Perkins No. 2.....	Slightly musty, sour, strongly aromatic.	Very pleasant, flowery.
Ukiah.....	Strongly aromatic.....	Strongly aromatic.....	Slightly fatty, aromatic.
Wheatland.....	Strongly aromatic, disagreeable.	Strongly aromatic, pleasant, characteristic.	Strongly aromatic, not agreeable.
Oregon.....	Extremely strong aromatic, not agreeable.	Strongly aromatic, slightly musty.	Strongly aromatic, pleasant.
New York.....	Strong, characteristic, not agreeable.	Musty and unpleasant, aromatic.	Strongly aromatic, not agreeable.
Washington.....	Agreeable and strongly aromatic.	Agreeable and aromatic.
Imported (Saaz).....	Mild, aromatic, agreeable.	Very pleasant, characteristic.	Pleasant, mild, characteristic.
TASTE.			
California:			
Perkins No. 1.....	Slightly fatty, slightly pungent.	Slightly pungent, slightly bitter.	Slightly pungent, slightly bitter.
Cosumne.....	Aromatic, not pungent, slightly bitter.	Fatty, slightly bitter, aromatic.	Fatty, bitter, pungent.
Perkins No. 2.....	Slightly fatty, aromatic, faintly pungent.	Slightly fatty, bitter, faintly pungent.
Ukiah.....	Bitter, slightly pungent, aromatic.	Fatty, slightly pungent, aromatic.	Fatty, becoming aromatic and bitter.
Wheatland.....	Bitter, aromatic, slightly pungent.	Bitter, aromatic, slightly pungent.	Fatty, slightly bitter, pungent.
Oregon.....	Slightly pungent, becoming slightly bitter.	Fatty, becoming slightly bitter.	Slightly fatty, slightly bitter.
New York.....	Bitter, aromatic, not pungent.	Slightly fatty and bitter, slightly pungent.	Slightly sour, slightly bitter and pungent.
Washington.....	Slightly fatty and bitter, very little pungency.	Slightly bitter, slightly pungent.
Imported (Saaz).....	Fatty, slightly bitter, not pungent.	Fatty, aromatic, slightly pungent.	Fatty, aromatic, very slightly pungent.

TABLE II.—Physical properties of various hop oils distilled during several successive seasons—Continued.

SPECIFIC GRAVITY AND INDEX OF REFRACTION.

Source of hops.	Specific gravity, 20° C.			Index of refraction at 20° C.		
	1907 crop.	1908 crop.	1909 crop.	1907 crop.	1908 crop.	1909 crop.
California:						
Perkins No. 1.....	0.821	0.838	0.8316	1.4838	1.4783	1.4716
Cosumne.....	.821	a. 8395	.842	1.4825	1.4724	1.4733
Perkins No. 2.....		a. 8289	.8422		1.4691	1.4743
Ukiah.....	.821	a. 831	a. 839	1.4890	1.4737	1.4718
Wheatland.....	.828	.8443	.8358	1.4870	1.4753	1.4743
Oregon.....	.8343	.838	.8433	1.4802	1.4730	1.4705
New York.....	b. 859	b. 834	b. 8747	1.4804	1.4756	1.4800
Washington.....		.850	.8464		1.4763	1.4734
Imported (Saaz).....	b. 852	b. 821	b. 858	1.4905	1.4852	1.4829

a Specific gravity at 23° C.

b Specific gravity at 24° C.

SOLUBILITY.^a

[Quantity of oil dissolved in 3 volumes of 94 per cent alcohol.]

Source of hops.	1907 crop.	1908 crop.	1909 crop.
California:			
Perkins No. 1..	0.55 volume oil, turbid, yellowish residue.	0.7 volume oil, turbid.	0.8 volume oil.
Cosumne.....	0.5 volume oil, whitish residue.	0.85 volume oil, brownish residue.	Do.
Perkins No. 2..		0.7 volume oil, turbid.	0.75 volume oil, slightly turbid.
Ukiah.....	0.35 volume oil, slight turbidity, yellowish-brown residue.	0.85 volume oil, turbid.	0.95 volume oil, slightly turbid, with reddish residue.
Wheatland....	0.35 volume oil, turbid, yellowish residue.	0.75 volume oil, brown residue.	0.7 volume oil.
Oregon.....	0.65 volume oil, turbid, yellow residue.	0.9 volume oil.....	1 volume oil.
New York.....	0.85 volume oil, brown residue.	0.85 volume oil.....	0.8 volume oil, light brown.
Washington.....		0.85 volume oil, turbid.	0.9 volume oil.
Imported (Saaz)...	0.75 volume oil, slightly turbid.	0.5 volume oil, yellow viscous residue.	0.75 volume oil, slightly turbid, bark-brown, viscous residue.

^a Solubility of 1907 crop determined after two years; 1908 crop determined after one year.

Color, odor, and taste, which appeal solely to the senses, are not especially significant. The colors of the various oils, ranging from a golden yellow to a dark brown, were due largely to the condition of the material and the time of the distillation. The first runnings obtained in all of the distillations were nearly colorless, but gradually deepened in color as the distillation progressed. The predominant colors seemed to be red and brown, the golden-yellow color being obtained only when small quantities of hops were distilled on a small laboratory scale. Whenever large quantities (100 to 200 pounds) were distilled, the resulting oil invariably possessed a dark color, the particular tint varying with the season. No constant difference was observed in oils from the various sources.

The odor in all cases was naturally characteristic of hops. In some instances, however, a slightly musty odor was perceptible. The oils from the American hops were all strongly aromatic and in most cases agreeable. A slight yet distinctly musty odor was perceived in several of the oils, due probably to imperfect drying and subsequent sweating of the hops in the bale. The oils from the foreign hops seemed to be distinctly different from the American oils, possessing a very pronounced flowery odor, combined with a fatty odor, the effect being most agreeable.

The sense of taste, which is influenced directly by the sense of smell, is generally capable of distinguishing definite and characteristic qualities of a substance, such as pungency and bitterness. Acidity and fattiness can also be easily detected. All of the oils in question had a decidedly aromatic taste, and there were also a number in which bitterness, fattiness, and acidity were very pronounced. The oils from the California hops were all characterized by bitterness and pungency, with slight fattiness. The oils from the imported hops were strongly fatty with only very slight bitterness and pungency.

The densities of the California oils bore a close relationship during individual seasons, differing somewhat from season to season. This would seem to indicate that the approximate composition during any one season was about the same in the several oils. The average specific gravity of the several California oils for the three seasons was about 0.8326. It will be seen that the Oregon oils were somewhat higher, the average being 0.8385. The oils from the imported hops, with an average specific gravity of 0.8433, and the Washington oils, with an average of 0.8482, followed in order. The oils with the highest general specific gravity were those from the New York hops, which averaged 0.8554 at 24° C. This figure would be increased if corrected to the temperature at which the specific gravity of the majority of the oils was recorded. It is generally acknowledged that the specific gravity is modified by the composition of an oil, but it is doubtful whether the differences noted above would cause any remarkable change in the quality of the oil. A

high specific gravity would usually be accompanied by a larger percentage of high-boiling constituents, and vice versa.

From Table II it is readily seen that the refraction of the California oils during each of the three years shows but little variation. During the successive seasons the refraction of the oils from the 1907 crop was somewhat higher than that of the two following years. This was accounted for by the fact that the index of refraction of the oils of the 1907 crop was taken about two years later (1909), showing that a change had taken place in the oils. The refractive property of the Oregon, New York, and Washington oils, as compared with the California oils, was not greatly different. However, the oils from the imported hops showed a higher refractive index than any of the other oils. This, again, may be due to the presence of a somewhat higher percentage of highly refractive constituents in these oils.

The solubility of a volatile oil in alcohol depends upon the composition of the oil. A high percentage of terpenes and sesquiterpenes decreases the solubility and a high content of oxygenated compounds increases it. Owing to the insolubility of hops oils in alcohol and the difficulty thereby encountered in obtaining comparative results, a deviation was made from the usual method employed for determining solubility. One volume of the oil was thoroughly shaken with three volumes of 94 per cent alcohol in a graduated cylinder, after which the resinous insoluble matter was centrifuged. The amount of insoluble matter could then be easily read on the bottom of the cylinder and the percentage of dissolved material readily calculated.

Apparently the most soluble oil among the number was the oil from the Oregon hops, one volume of oil from the 1909 crop dissolving completely in three volumes of 94 per cent alcohol, the oil from the 1908 crop being almost as soluble. Washington and New York oils from the crops of 1908 and 1909 were slightly less soluble than the Oregon oils. The California oils of these two seasons were a trifle less soluble than those from the Washington and New York hops, while the imported oils appeared to be the least soluble.

The much lower solubility of the 1907 oils was due to the fact that the determinations were not made until two years after distillation. Although the oils had been kept in well-filled bottles and well protected from the light, decomposition had ensued, which resulted in the formation of less soluble constituents, thus decreasing the solubility of the oils. This plainly shows the effect of age on the solubility of the oils.

From the information thus obtained it would appear that the oils with the highest solubility probably contained a larger percentage of oxygenated compounds and a lower percentage of terpenic compounds than the less soluble oils.

CHEMICAL PROPERTIES OF THE VARIOUS OILS

In order to make a better comparison of the several oils with regard to their aromatic quality, determinations were made of the acid, ester, and saponification numbers. These constants are usually ascertained in order to get some idea of the odoriferous constituents.

The determination of the acid number is readily accomplished by simple titration with standard alkali and is expressed by the number of milligrams of potassium hydroxid required to neutralize the free acidity contained in 1 gram of the oil. A number of factors may tend to influence this value. Freshly distilled oils, in most instances, are low in free acidity, while old oils or oils distilled from old material usually possess a larger quantity of free acids. Improper conditions of drying and storing have a tendency to cause changes to take place in the aromatic compounds, which result in the formation of free acids, and thereby increase the acid numbers.

As previously stated, the esters, which consist of combinations of acids and alcohols, are considered the odor bearers. These values are easily determined by saponifying the oil with alcoholic alkali and calculating the number of milligrams of potassium hydroxid consumed in the reaction by 1 gram of oil. This represents an accurate measurement of the ester constituents. As in the case of free acidity, this value may also be affected by conditions under which the material is dried and stored. The stage of growth and development of the plant is also a strong factor in modifying the ester content of volatile oils.

The saponification number represents the total amount of alkali, expressed in milligrams, necessary to react completely with 1 gram of oil, being the sum of the acid and ester numbers.

These constants which are so directly related to the odor were carefully determined for each of the hop oils distilled from the various samples of hops. A determination of the free alcohols in these oils was also made, but was barren of results in all cases. Acetylation with acetic-acid anhydrid with subsequent saponification is necessary and is readily accomplished in many oils. However, the nature of some alcohols is such that a quantitative acetylation is impossible, owing to decomposition when boiled with the acetic-acid anhydrid. Modification of the usual method, altering the length of boiling and the quantity of acetic anhydrid, gave negative results in all cases. From this peculiar behavior of the oil it is inferred that either the oils have no free alcohol compounds or that the alcohol compounds, if present, are of such a nature as to be incapable of quantitative acetylation.

The acid, ester, and saponification numbers of the oils from the American and foreign hops are recorded in Table III.

TABLE III.—The acid, ester, and saponification numbers of hop oils distilled during several seasons.

Sources of hops.	Acid numbers.						Ester numbers.						Saponification numbers.					
	1906	1907	1908	1909	1910	Average.	1906	1907	1908	1909	1910	Average.	1906	1907	1908	1909	1910	Average.
California:																		
Perkins No. 1.....	0.0	1.5	1.1			0.86	42.0	47.0	47.1			45.5	42.0	48.5	48.2			46.2
Cosumme.....	0	2.4	2.9			1.76	45.0	46.0	51.0			47.3	45.0	48.4	53.9			49.1
Perkins No. 2.....		1.6	2.0			1.80		45.0	43.7			44.3		46.0	45.7			46.1
Ukiah.....	0	1.1	1.8			.96	40.8	44.0	51.0			45.2	40.8	45.1	52.8			46.2
Wheatland.....	2.3	2.0	1.4			1.90	50.0	45.5	41.0			45.5	52.3	47.5	52.4			47.4
Oregon.....	5.5	1.6	1.0	2.8		2.70	72.0	57.0	50.2	56.0		58.8	77.5	58.0	51.2	58.8		61.5
New York.....	4.8	3.6	2.1	2.5		3.25	44.0	61.0	47.0	51.8		50.9	48.8	64.6	49.1	54.3		54.2
Washington.....		1.0	1.5			1.25		51.8	53.8			52.8		52.8	53.3			54.0
Imported (Saaz).....	1.5	1.5	1.0	3.0	3.1	2.02	12.6	20.0	36.0	28.6	20.4	23.5	14.1	21.5	37.0	31.6	23.5	21.1

The oils, in the order of their average acidity, were as follows: New York, Oregon, imported, California, and Washington. In every instance the New York oils showed comparatively high acidity. Whether this high acidity content was inherent in the oil or whether it was due to conditions of drying and storing can not be stated. The high acidity seemed to be general, since two other samples of New York hops (not recorded) yielded oils with the acid numbers 2.6 and 3.2, respectively. The average acidity of the Oregon hop oil as given is probably somewhat high, as it was considerably augmented by the high acid number of the oil from the 1906 crop, which was distilled from a sample of hops that were not in as fresh condition as the 1907, 1908, and 1909 hops. The oils from the imported hops were somewhat lower than those from the Oregon hops, being fairly constant in 1906, 1907, and 1908, but much higher in 1909 and 1910. These were followed by the California and Washington oils, with an average of 1.41 and 1.25, respectively.

The high and low acid numbers were significant of nothing important as far as the aroma was concerned, as the free acidity did not perceptibly affect the odor of the oil.

The ester numbers revealed most striking similarities and dissimilarities, not only during one season but for several successive seasons. It was to be expected that the oils from the hops during any one season would show differences, but that these same differences should appear during three, four, and even five successive seasons was most surprising.

The oils from the imported hops were conspicuous because of the fact that the data for the several seasons showed the ester content to be only about one-half as great as the ester content of the oils from the California, Oregon, Washington, and New York hops. Besides the samples recorded in the table, a cold-storage sample of Saaz hops of the 1906 crop, distilled one year later, gave an oil with an ester number of

24. Three samples of Dauber, Auscher, and Oesterreich Gewächshops of the 1910 crop possessed the ester numbers 15.7, 21.3, and 18, respectively. Figure 1 shows that the nine samples of foreign oils were uniformly lower in esters than the American oils.

The close relationship of the ester numbers of the California oils during the seasons of 1907, 1908, and 1909 is very evident. The general average ester number of the California oils was 45.5, as compared with 50.9 for New York, 52.8 for Washington, 58.8 for Oregon, and 23.5 for the imported. No important difference was noted in the various California oils. This is true also of the Washington oils, which, however, were distilled during only two seasons. The ester content of the Oregon oils averaged considerably higher than the oils from any of the other hops and, with the exception of the oil from the 1906 crop, the history of which was doubtful, the oils bear close relationship from year to year. The New York oils were slightly more variable, but nevertheless occupy about the same relative position from year to year with respect to the other oils.

In the case of the foreign oils, the ester numbers, which are a measure of the odorous constituents, would seem to point to a consistently lower content of these compounds. That this unusually low ester content is responsible for the generally acknowledged superior aroma of imported hops can not be positively stated, although it is highly probable, since it is known that other oils with a low ester content, notably lavender and peppermint oils, are more agreeable and fragrant than oils with a high ester content.

The saponification numbers, which represent the total acids and esters in the oils, presented practically the same constant differences and similarities brought out by comparison of the ester numbers.

While it is not known whether the ester numbers would continue lower indefinitely in case of the foreign oils, it may be assumed that such would probably be the case, since the authentic samples distilled during the five seasons showed abnormally low values as compared with the American oils. In like manner, it may also be assumed that the high ester numbers of the American oils would continue indefinitely, since they were fairly constant during the three seasons in which the experiments were carried on.

FRACTIONATION OF THE VARIOUS OILS

Since volatile oils are composed of a number of constituents with boiling points which often vary considerably, fractional distillation has proved a useful and effective method for the partial separation of these constituents. Ordinarily a straight-neck distilling flask with side tube is used for this purpose, the bulb of the thermometer being placed immediately opposite the mouth of the tube and the fractions collected at different intervals. By this means a partial separation of the con-

stituents is accomplished. A better separation, however, can be made by means of a 3-bulb Ladenburg distilling flask, which is a flask with

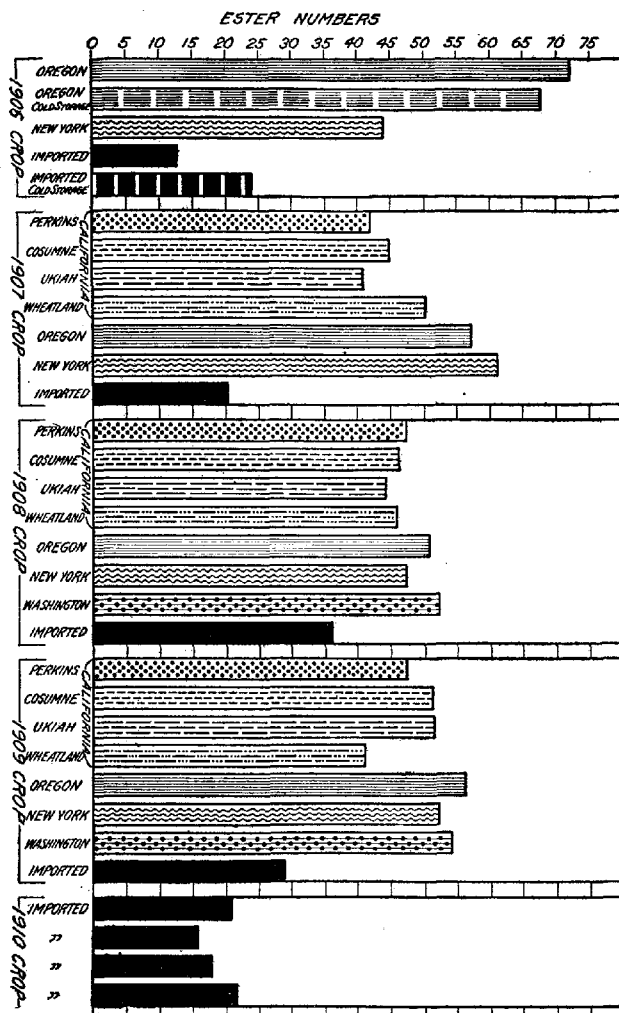


FIG. 1.—Relative ester content of various hop oils.

three bulbs blown in the neck below the side tube and the flask proper. These bulbs act like a distilling column, causing a more complete sepa-

ration of each of the constituents of the oil. In the fractionation of the various hop oils, a flask of this sort having a capacity of 200 cubic centimeters was employed. The bulb of the thermometer was placed directly opposite the outlet tube in all the experiments. The rapidity of distillation was also regulated so that about the same amount of oil distilled during a given period of time. Fractions were collected between different temperatures, the same range of temperature being maintained in the distillation of each oil. Even with all these precautions it was impossible to make the separation of the compounds entirely complete. Vacuum distillation would possibly have effected the separation with less decomposition, but the difficulty of keeping conditions alike in each case would hardly compensate for the partial decomposition which is unavoidable by direct distillation. With the conditions of distillation practically alike in each fractionation, approximately the same amount of decomposition should result in the high-boiling fractions in each oil.

For purposes of comparison, fractionation by direct distillation was employed with each sample of oil from the various kinds of hops, seven fractions being collected from the oil of the 1906 crop, as follows: Fraction 1, 165° to 185° C.; fraction 2, 185° to 205° C.; fraction 3, 205° to 225° C.; fraction 4, 225° to 245° C.; fraction 5, 245° to 260° C.; fraction 6, 260° to 275° C.; fraction 7, 275° to 290° C.; and finally the residue 290° C. +. Seven fractions were also collected from the oils of the 1907, 1908, and 1909 crops between somewhat different temperatures, as will be seen in the tables. The percentage of oil distilled was calculated for each fraction of the various oils of the crops of 1906, 1907, 1908, and 1909.

In order to facilitate comparisons and to bring out more forcibly the differences in the approximate composition of the oils, as manifested by the fractionation, tabulations were made of the oils distilled each season. The figures in Table IV express the percentage of oil distilled at the temperatures indicated. Curves were also made of each fractionation in order that the comparison could be seen at a glance (see figs. 2, 3, 4, and 5).

TABLE IV.—*Fractionation of hop oils, showing the percentage distilled at different temperatures for the years 1906 to 1909, inclusive.*

1906 CROP.								
Source of hops.	Fraction 1, 165° to 185° C.	Fraction 2, 185° to 205° C.	Fraction 3, 205° to 225° C.	Fraction 4, 225° to 245° C.	Fraction 5, 245° to 260° C.	Fraction 6, 260° to 275° C.	Fraction 7, 275° C. +	Residue, 290° C. +
Oregon.....	26.9	13.1	11.55	14.7	9.2	10.3	14.25
Do. ^a	33.5	11.4	6.4	5.7	7.9	6.4	12.4	16.0
New York....	24.5	17.5	2.5	3.5	15.2	19.2	17.6
Imported								
(Saaz)....	9.0	9.1	2.5	8.4	25.6	27.8	17.6
Do. ^a	10.0	9.2	8.5	10.0	30.0	18.6	5.7	8.0

^a In cold storage one year before distillation of the oil.

TABLE IV.—Fractionation of hop oils, showing the percentage distilled at different temperatures for the years 1906 to 1909, inclusive—Continued.

Source of hops.	1907 CROP.							Residue, 290° C.
	Fraction 1, 165° C.	Fraction 2, 165° C. to 170° C.	Fraction 3, 170° C. to 185° C.	Fraction 4, 185° C. to 225° C.	Fraction 5, 225° C. to 260° C.	Fraction 6, 260° C. to 275° C.	Fraction 7, 275° C. to 290° C.	
California:								
Perkins.....	18.7	26.5	18.7	7.5	5.0	5.0	10.6	8.1
Cosumne.....	24.3	15.0	14.3	5.0	3.1	7.5	14.3	16.5
Ukiah.....	22.0	29.0	9.0	6.7	4.0	3.2	11.5	14.6
Wheatland.....	19.0	16.0	18.5	12.0	11.0	6.0	9.0	8.5
Oregon.....	5.5	14.0	25.0	14.5	13.0	6.5	9.5	12.0
New York.....	.0	5.7	15.7	18.8	22.8	11.0	12.8	13.2
Imported (Saaz).....	.0	1.7	10.0	20.5	30.0	9.1	10.7	18.0
1908 CROP.								
California:								
Perkins.....	3.5	6.5	25.0	14.5	13.0	4.5	14.5	18.5
Cosumne.....	6.5	11.5	32.0	18.0	11.6	6.0	8.0	15.8
Ukiah.....	6.0	16.3	23.6	14.8	7.2	8.0	8.3	15.8
Wheatland.....	4.0	11.7	27.4	17.4	12.5	9.3	8.7	9.0
Oregon.....	7.0	7.7	23.0	20.0	17.0	8.8	6.0	8.0
New York.....	3.1	15.3	25.3	18.8	16.6	6.8	6.0	8.0
Washington.....	3.5	4.0	12.7	20.0	18.0	13.3	11.5	17.0
Imported (Saaz).....	4.9	13.3	24.4	15.3	7.7	5.3	10.7	18.1
1909 CROP.								
California:								
Perkins.....	2.5	7.0	15.0	10.0	7.5	15.4	23.4	19.2
Cosumne.....	5.4	4.3	9.1	12.5	13.0	14.6	21.2	19.9
Ukiah.....	3.5	11.5	21.5	20.0	12.0	7.5	12.0	12.0
Wheatland.....	4.1	5.8	20.8	15.4	6.6	5.4	20.0	21.9
Oregon.....	4.1	8.3	20.8	21.4	15.8	9.1	7.5	13.0
New York.....	5.0	6.5	11.0	8.5	18.0	11.0	13.1	26.0
Washington.....	3.7	7.2	19.0	21.5	16.5	8.8	10.6	12.7
Imported (Saaz).....	4.2	5.4	10.6	25.0	13.2	15.2	26.4	

COMPARISON OF FRACTIONATED OILS

As shown by Table IV and figure 2, the fractionation of the oils from the Oregon cold storage and Oregon and New York hops follow entirely different lines from the imported and the cold-storage imported hops. In case of the first three, fraction 1 (165° to 185° C.) represents the major portion of the oil, while the oils from the imported hops are directly the reverse, fractions 5 (245° to 260° C.) and 6 (260° to 275° C.) representing more than one-half of the oils. These results indicate that the oils from

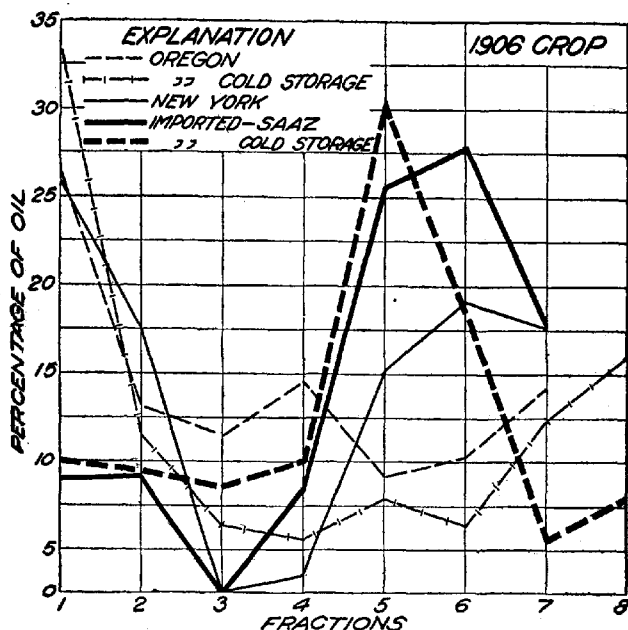


FIG. 2.—Fractionation curves of hop oils from the crops of 1906.

the American hops of the 1906 crop are richest in the low-boiling constituents and the imported oils from the same year are richest in the high-boiling constituents.

The fractionation of the oils of the 1907 crops, as shown also in Table IV and in figure 3, bears out practically the same conclusions. Fractions 1, 2, and 3 (165° , 165° to 170° , and 170° to 185° C.) of the California oils comprise from 53 to 63 per cent of the original oils, and of the Oregon oil nearly 45 per cent, while the same three fractions of the New York oil correspond to 21 per cent of the original oil. The portion of the imported

oil distilling below 185°C. was only 11.7 per cent of the oil. These results again show the deficiency of the imported oil in the low-boiling constituents. When fractions 4 (185° to 225°C.) and 5 (225° to 260°C.) are considered the reverse conditions exist, these fractions of the imported oils representing about 50 per cent of the oil, 41 per cent of the New York oil, 27 per cent of the Oregon oil, and an average of 13 per cent of the California oils. The curves of the remaining fractions are very similar. The figure shows that the imported oil follows almost a directly reverse course from that of the California and Oregon oils. In this respect the New York oil seems to be the most closely related to the foreign oil.

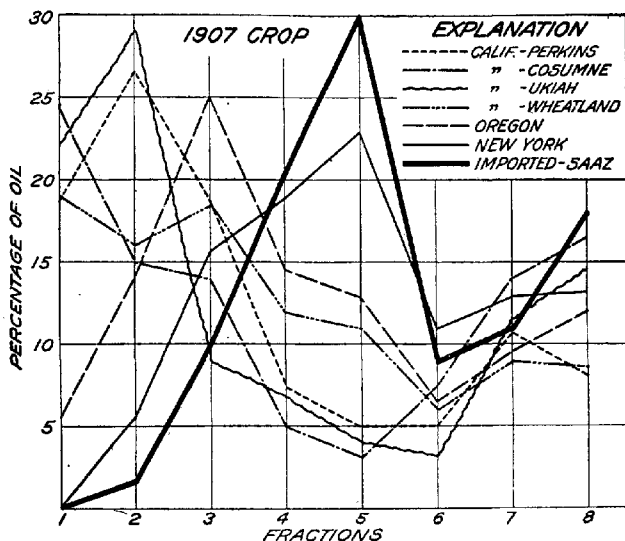


FIG. 3.—Fractionation curves of hop oils from the crops of 1907.

Comparing the various oils of the 1908 crop, as given in Table IV and the curves in figure 4, it will be seen that nearly all show a similar trend in their fractionation properties. The California oils, on an average, again surpass the other oils in constituents which boil below 185°C. , the lowest in this respect being those from Washington and Oregon. In that year, for the first time in the three seasons, the fractionation curve of the imported oil followed lines somewhat similar to those of the American oils. No explanation is ventured for this change in the imported oil.

The difference between the imported oil and the other oils of the 1909 crops is also very noticeable in Table IV and figure 5. The California oils of the 1909 crop, as in 1906, 1907, and 1908, distilled over largely in the

first four fractions, the Cosumne oil showing slight deviation. The curve of the first four fractions of the imported oil is again far below that of any of the other oils. From fraction 4 the New York oil follows a similar course to that of the imported oil. Fraction 5 (225° to 260° C.), in both the imported and the New York oils, shows the highest percentage. The similarity of the Oregon and Washington oils is noteworthy, both curves following almost identical lines.

As a general thing, it will be observed that the oils from the California, Oregon, and Washington hops during the several seasons showed a high

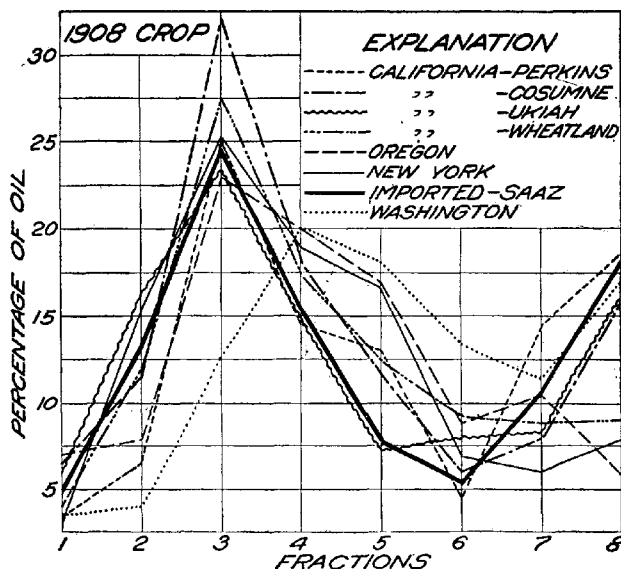


FIG. 4.—Fractionation curves of hop oils from the crops of 1908.

content of low-boiling constituents, while the oils from the imported hops were invariably poorer in the low-boiling constituents. On the other hand, the oils from the imported hops seemed, generally speaking, to contain much higher percentages of the high-boiling compounds, as shown by fractions 4 and 5; the oil of the 1908 crop, however, was unique in that it appeared to be similar to the other oils during that particular season. The curves of the imported oils followed those of the New York oils the most closely, the general direction being similar. The California oils also followed very similar directions, as did the Oregon and Washington oils.

PHYSICAL PROPERTIES OF THE FRACTIONS

SPECIFIC GRAVITY

Although the specific gravity, as a rule, is apt to show only slight differences, owing to the variable composition of the oil, it was thought that determinations of this property might be of some value. The specific gravity of the various fractions from the oils of the crops of 1906, 1907, 1908, and 1909 is given in Table V.

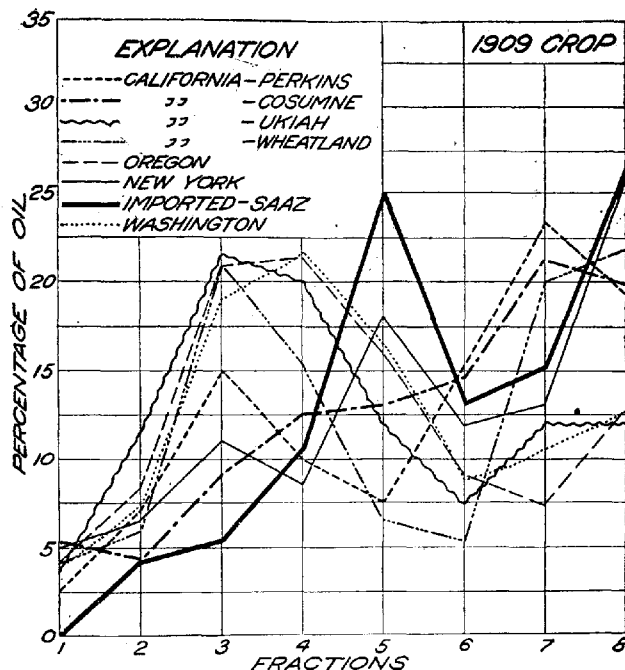


FIG. 5.—Fractionation curves of hop oils from the crops of 1909.

TABLE V.—Specific gravity of fractions of hop oils for the years 1906 to 1909, inclusive.
1906 CROP (AT 25° C.).

Source of hops.	Fraction 1, 16° to 18° C.	Fraction 2, 18° to 20° C.	Fraction 3, 20° to 22° C.	Fraction 4, 22° to 24° C.	Fraction 5, 24° to 26° C.	Fraction 6, 26° to 27° C.	Fraction 7, 27° C.
Oregon.....	0.818	0.821	0.849	0.876	0.877	0.881
Do. ^a820	.839	.859	.882	.894	.900	0.887
New York.....	.813	.829	.853	.862	.890	.894
Imported.....	.815	.819	.825	.835	.888	.888
Do. ^a826	.838	.850	.873	.891	.896	.836

^a In cold storage one year before distillation.

TABLE V.—*Specific gravity of fractions of hop oils for the years 1906 to 1909, inclusive—Continued.*

1907 CROP (AT 25° C.).							
Source of hops.	Fraction 1, —165° C.	Fraction 2, 165° C. to 170° C.	Fraction 3, 170° C. to 185° C.	Fraction 4, 185° C. to 225° C.	Fraction 5, 225° C. to 260° C.	Fraction 6, 260° C. to 275° C.	Fraction 7, 275° C. to 290° C.
California:							
Perkins.....	0.803	0.806	0.815	0.843	0.875	0.889	0.876
Cosumne.....	.809	.811	.819	.840	.875	.871	.862
Ukiah.....	.806	.810	.824	.848	.881	.891	.881
Wheatland.....	.809	.810	.816	.845	.893	.900	.895
Oregon.....	.809	.811	.816	.855	.889	.895	.876
New York.....		.812	.821	.853	.884	.891	.876
Imported (Saaz).....			.812	.832	.874	.887	.878
1908 CROP (AT 23° C.).							
California:							
Perkins.....	0.802	0.805	0.809	0.834	0.883	0.871	0.866
Cosumne.....	.805	.804	.810	.835	.884	.894	.880
Ukiah.....	.803	.804	.808	.835	.882	.888	.863
Wheatland.....	.805	.806	.811	.837	.885	.894	.882
Oregon.....	.802	.801	.806	.828	.885	.890	.883
New York.....		.810	.813	.842	.889	.897	.897
Washington.....	.803	.805	.809	.835	.881	.887	.874
Imported (Saaz).....		.811	.813	.840	.885	.890	.876
1909 CROP (AT 23° C.).							
California:							
Perkins.....	0.812	0.815	0.821	0.844	0.879	0.863	0.876
Cosumne.....	.820	.822	.832	.855	.891	.888	.875
Ukiah.....	.806	.807	.810	.833	.873	.891	.881
Wheatland.....	.803	.807	.812	.831	.872	.872	.888
Oregon.....	.806	.806	.811	.831	.880	.894	.889
New York.....	.823	.819	.828	.859	.890	.900	.886
Washington.....	.808	.808	.813	.836	.884	.895	.883
Imported (Saaz).....		.810	.816	.837	.876	.882	.872

The specific gravity, although less inclined to indicate material differences, at least conveys some idea of the composition of the succeeding fractions. The low-boiling fractions naturally possess the lowest specific gravity, which increases as the constituents of greater density make their appearance in the later fractions. When the specific gravity is fairly constant the fractions may contain similar constituents in similar proportions. A rapid rise during distillation signifies a quick change and a sharp separation of the denser compounds. Sudden increases in specific

gravity from fraction to fraction, as observed in the table, may be construed to mean that a fairly good separation of the denser compounds has taken place. The fractions of the lowest specific gravity in all cases were those boiling below 185°C . This portion of the oil should contain the terpenic constituents if present. Fractions 1, 2, and 3 did not differ greatly from each other through the four seasons, thus indicating a similar composition of the oils. The specific gravity of the oils from the cold-storage samples was greatly different from that of the other oils, being higher in all cases than in the oils from the fresh hops. The specific gravity of fractions 4, 5, and 6 increased very much in the sequence in which they were distilled, comparing very favorably, however, in the different oils. The oxygenated constituents, if present in the oil, would possibly be found largely in fractions 4 and 5, while fractions 6 and 7 should contain sesquiterpene constituents. Fraction 7 showed a decrease in specific gravity, due probably to partial decomposition at the high temperature at which it was distilled.

Curves of the specific gravity were not drawn because of the similarity in the various fractions, the same general course being evident in each oil. In general, the table of results shows that the fractionation of each oil proceeded about the same with regard to the nature of the constituents which distilled over. Although the specific gravities corresponded very closely, it is not necessarily inferred that the oils are alike in composition. The difference may be quantitative rather than qualitative, the size of the fractions determining the quantitative composition of the oils.

OPTICAL ROTATION

The value of the property of optical rotation, though important in most volatile oils, is perhaps lessened when applied to oil of hops, since its constituents are more or less inactive or only slightly active. The rotatory power of each fraction of the oils was carefully determined, and as it was low it was expressed in minutes rather than degrees. The results were tabulated for each season (Table VI) and curves were drawn to facilitate the comparison (figs. 6, 7, 8, and 9).

TABLE VI.—*Specific rotation of hop oils distilled for the years 1906 to 1909, inclusive.*

1906 CROP.

Source of hops.	Fraction 1, 165° to 185°C .	Fraction 2, 185° to 205°C .	Fraction 3, 205° to 225°C .	Fraction 4, 225° to 245°C .	Fraction 5, 245° to 260°C .	Fraction 6, 260° to 275°C .	Fraction 7, 275°C .
	Minutes.	Minutes.	Minutes.	Minutes.	Minutes.	Minutes.	Minutes.
Oregon.....	- 7.6	-20.7	-15.9	+ 9.4	+47.0	+89.2
Do. ^a	Inactive	-12.3	-25.1	-44.6	+27.8	+49.9	+114.5
New York.....	-11.7	-15.8	+42.5	+60.1	+34.9	+52.5
Imported.....	Inactive	Inactive	+60.0	+36.6	+63.0	+35.9
Do. ^a	Inactive	- 4.9	-11.1	-14.2	+11.6	+67.5	+177.7

^a In cold storage 1 year before distillation.

TABLE VI.—Specific rotation of fractions of hop oils distilled for the years 1906 to 1909, inclusive—Continued.

1907 CROP.							
Source of hops.	Fraction 1, -165° C.	Fraction 2, 165° to 170° C.	Fraction 3, 170° to 185° C.	Fraction 4, 185° to 225° C.	Fraction 5, 225° to 260° C.	Fraction 6, 260° to 275° C.	Fraction 7, 275° to 290° C.
California:	Minutes.	Minutes.	Minutes.	Minutes.	Minutes.	Minutes.	Minutes.
Perkins.....	-15.0	-17.7	-27.3	-56.3	-68.8	-87.1	-35.9
Cosumne.....	-12.7	-23.6	-35.2	-43.2	-54.5	+33.2	+38.4
Ukiah.....	-12.8	-22.7	-35.2	-66.0	-70.8	-37.3	+47.1
Wheatland.....	-12.7	-24.7	-36.4	-29.4	-58.7	-69.1	+139.0
Oregon.....	-3.8	-5.7	-16.9	-38.3	-63.0	+25.5	+58.7
New York.....			-5.8	-9.4	+10.5	+59.7	+93.1
Imported (Saaz).....			Inactive	-4.6	+1.7	+9.2	+66.9
1908 CROP.							
California:							
Perkins.....	Inactive	Inactive	-20.5	-44.6	-66.5	+28.4	+28.4
Cosumne.....	-25.5	-25.6	-28.8	-44.5	-72.6	-40.0	+23.4
Ukiah.....	Inactive	-6.2	-10.6	-39.5	-58.7	+14.7	
Wheatland.....	-25.5	-30.7	-38.2	-64.2	-84.3	-25.5	+28.1
Oregon.....	Inactive	-5.0	-16.1	-26.0	-13.1	+60.4	+9.5
New York.....		-17.7	-25.5	-27.0	+38.7	+88.5	+76.9
Washington.....		Inactive	-18.7	-27.3	+37.4	+79.3	+71.1
Imported (Saaz).....	Inactive	-15.2	-25.3	-44.7	+77.9	+104.7	+85.1
1909 CROP.							
California:							
Perkins.....	Inactive	-9.5	-24.8	-51.1	-66.9	4.8	23.9
Cosumne.....	-20.5	-24.8	-38.9	-63.0	-52.5	36.4	45.1
Ukiah.....		-13.8	-20.2	-39.6	-75.3	-41.6	21.1
Wheatland.....	-10.2	-14.3	-30.5	-54.8	-95.2	-70.0	9.6
Oregon.....	Inactive	Inactive	-10.6	-16.8	-14.0	83.4	107.2
New York.....		-15.1	-21.9	-29.3	-11.4	36.6	65.4
Washington.....		-14.8	-14.8	-32.5	8.3	99.6	104.1
Imported (Saaz).....				-17.1	-37.6	-13.9	47.4

Table VI and figures 6, 7, 8, and 9 show that the initial fractions, as a rule, were inactive. This is probably explained by the fact that these fractions consist of terpenes having little or no activity. The rotation of the first fractions was levo, the power to rotate to the left increasing in most cases up to the fifth fraction. This was par-

ticularly true of the California and Oregon oils of the crops of 1907, 1908, and 1909. The New York, Washington, and imported oils had a general tendency to manifest dextro rotation after the fourth fraction, the levo rotation of the former fractions being consistently less than the same fractions of the California and Oregon oils. The dextro rotation of the last three fractions seemed to be higher, in practically all cases, than

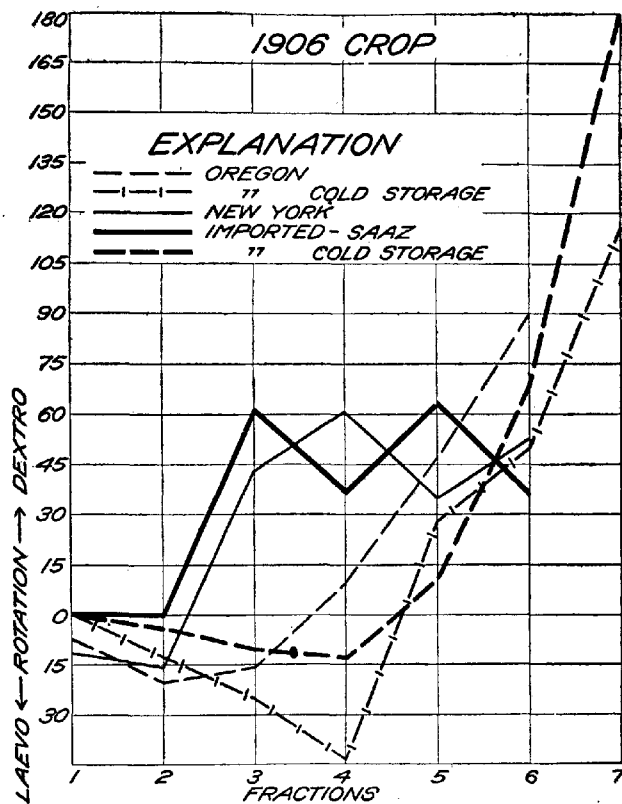


FIG. 6.—Optical-rotation curves of hop oils from the crops of 1906.

the same fractions of California oils. A most noticeable feature was the tendency of the New York oil to follow the same course as the imported oil during each season. The high-boiling portions of the oils, of which the esters and sesquiterpenes form a part, tended to show the greatest rotation. The curves of rotation, as well as the curves of fractionation, show some differences in the various oils, though perhaps in

a lesser degree. This difference appears to be fairly constant from season to season. The same general direction of the California oils during the three seasons is most striking. The curves of the oils of the

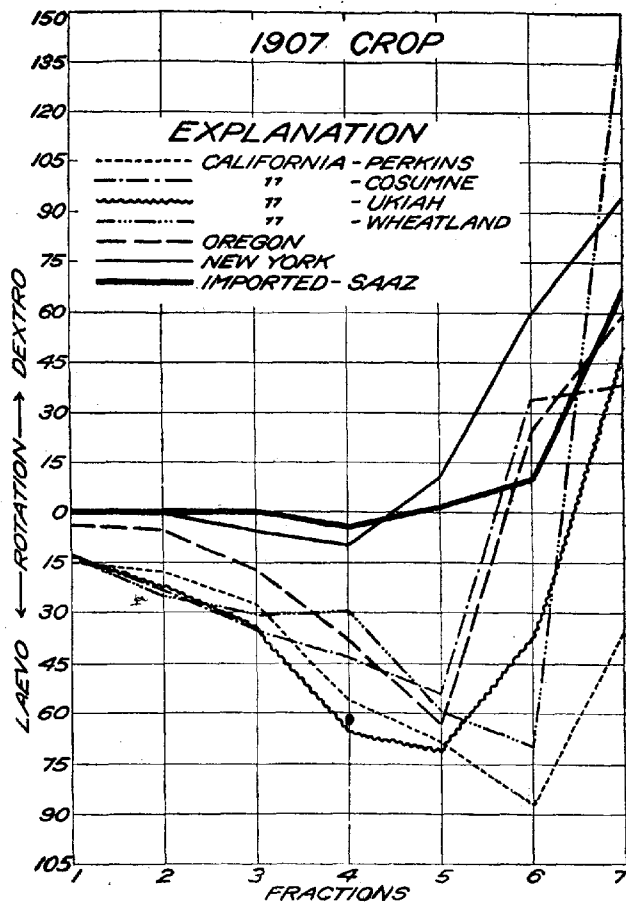


FIG. 7.—Optical-rotation curves of hop oils from the crops of 1907.

1906 crop further emphasize the strong dextro rotation of the oils from the foreign and New York hops as compared with the California and Oregon oils.

CHEMICAL PROPERTIES OF THE FRACTIONS
ACID, ESTER, AND SAPONIFICATION NUMBERS

The chemical properties of the oils and fractions are much more important in determining constant differences or similarities in the volatile oil of hops than the physical properties previously discussed. This is especially true of the aromatic quality of the oil, since quality is dependent upon the ester content. The ester content is expressed in the form

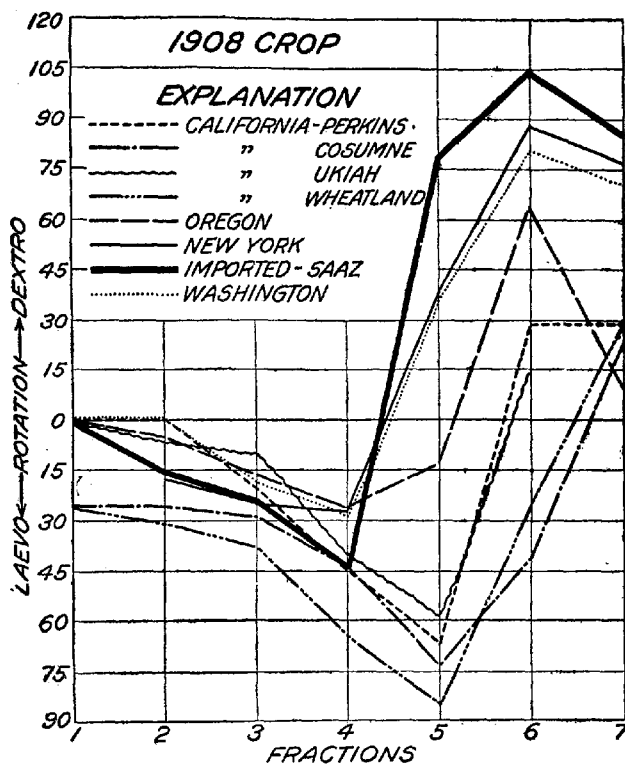


FIG. 8.—Optical-rotation curves of hop oils from the crops of 1908.

of ester numbers based on the amount of esters in 1 gram of the oil. The acid numbers of the fractions are less important, since these depend largely upon the extent of decomposition which the esters undergo during fractionation. Only a small amount of decomposition of the esters is required to liberate sufficient acid to produce high acid numbers, since, as has been shown, the acids in combination with the esters are those of high molecular weight. Owing to the consequent irregularity of the

acid numbers, only little importance can be attached to the results. The saponification numbers, which represent the total saponifiable constituents, including both free acids and esters, should exhibit practically no deviation from the course of the ester numbers. Particular stress is

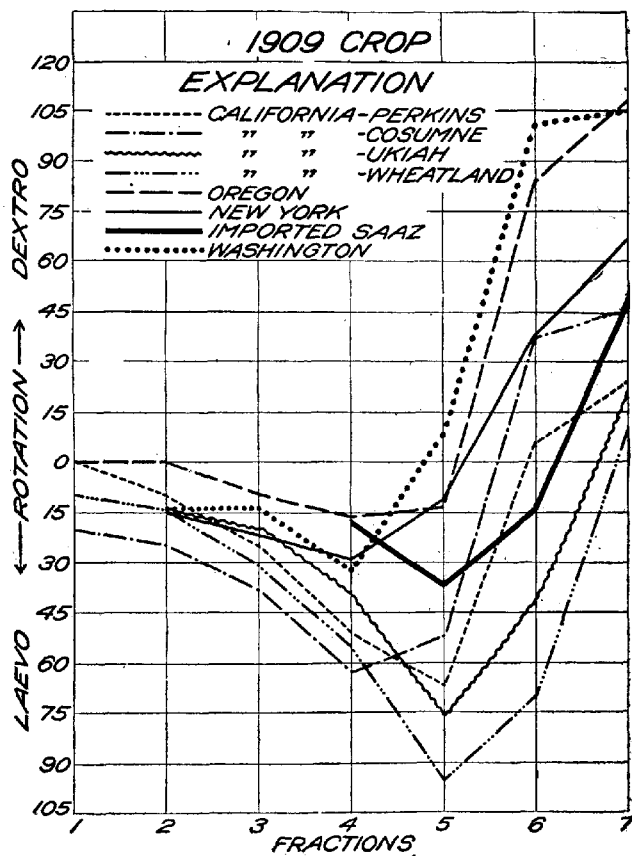


FIG. 9.—Optical-rotation curves of hop oils from the crops of 1909.

therefore placed upon the ester number of the fractions, since these values represent a measurement of the chief odorous constituents of the oils.

The acid, ester, and saponification numbers of the fractions from each individual oil of the seasons of 1906, 1907, 1908, and 1909 are shown in Table VII. Since particular attention is given to the ester numbers, curves were made of this chemical property of the fractions, as shown in figures 10, 11, 12, and 13.

TABLE VII.—Acid, ester, and saponification numbers of the various fractionated oils from hops for the years 1906 to 1909, inclusive.

1906 CROP.

Source of hops.	Fraction 1, 165° to 185° C.			Fraction 2, 185° to 205° C.			Fraction 3, 205° to 215° C.			Fraction 4, 225° to 245° C.			Fraction 5, 245° to 260° C.			Fraction 6, 260° to 275° C.			Fraction 7, 275° C.		
	Acid No.	Ester No.	Sap. No.	Acid No.	Ester No.	Sap. No.	Acid No.	Ester No.	Sap. No.	Acid No.	Ester No.	Sap. No.	Acid No.	Ester No.	Sap. No.	Acid No.	Ester No.	Sap. No.	Acid No.	Ester No.	Sap. No.
Oregon.....	0.0	143.0	143.0	6.9	94.0	100.9	8.0	104.0	112.0	10.8	79.0	89.8	6.6	53.3	99.9	7.7	23.0	30.7	8.2	0.0	8.2
Do. a.....	9.8	100.0	102.8	3.6	102.0	105.6	5.5	106.3	111.8	8.1	90.5	98.6	9.2	66.6	75.8	10.5	36.3	46.8	9.0	9.6	18.6
New York.....	0.0	84.4	84.4	3.7	70.0	73.7	14.0	79.0	93.0	8.2	41.0	40.2	7.9	23.0	30.9	5.1	14.3	19.4	7.4	0.0	7.4
Imported.....	3.8	39.0	42.8	6.9	31.8	38.7	7.9	79.0	86.9	5.3	29.3	34.6	2.5	7.6	10.1	2.1	0.0	2.1	0.0	0.0	0.0
Do. a.....	4.9	60.0	64.9	4.6	50.7	55.3	2.8	52.5	55.3	4.0	44.8	48.8	3.8	16.0	19.8	3.0	6.7	9.7	9.0	3.0	12.0

1907 CROP.

Source of hops.	Fraction 1, -165° C.			Fraction 2, 165° to 175° C.			Fraction 3, 175° to 185° C.			Fraction 4, 185° to 225° C.			Fraction 5, 225° to 260° C.			Fraction 6, 260° to 275° C.			Fraction 7, 275° to 300° C.		
	Acid No.	Ester No.	Sap. No.	Acid No.	Ester No.	Sap. No.	Acid No.	Ester No.	Sap. No.	Acid No.	Ester No.	Sap. No.	Acid No.	Ester No.	Sap. No.	Acid No.	Ester No.	Sap. No.	Acid No.	Ester No.	Sap. No.
California:	0.0	42.0	42.0	0.0	48.0	48.0	0.0	53.0	53.0	1.9	94.0	95.9	1.5	68.0	99.5	3.0	40.0	43.0	1.8	11.0	12.8
Perkins.....	0.0	61.0	61.0	0.0	65.0	65.0	0.0	69.0	69.0	1.7	86.0	90.7	0.0	64.0	64.0	1.8	21.0	22.8	0.0	3.5	3.5
Cosumme.....	0.0	44.0	44.0	0.0	46.5	46.5	0.0	61.0	61.0	0.0	70.0	70.0	3.0	58.0	61.0	5.1	38.0	43.1	2.7	10.6	13.3
Utah.....	2.5	53.5	56.0	1.3	54.0	55.3	1.9	58.5	60.4	2.9	66.2	72.1	4.8	48.0	54.8	6.6	18.0	24.6	7.7	5.0	12.7
Wheatland.....	2.4	62.7	65.1	1.6	65.0	66.6	1.3	68.8	70.1	1.9	91.7	103.6	2.9	75.6	78.5	4.7	27.4	32.1	4.3	10.3	14.6
Oregon.....	0.0	42.0	42.0	0.0	48.0	48.0	0.0	53.0	53.0	1.9	94.0	95.9	1.5	68.0	99.5	3.0	40.0	43.0	1.8	11.0	12.8
New York.....	0.0	44.0	44.0	0.0	46.5	46.5	0.0	61.0	61.0	0.0	70.0	70.0	3.0	58.0	61.0	5.1	38.0	43.1	2.7	10.6	13.3
Imported (Saaz).....	0.0	44.0	44.0	0.0	46.5	46.5	0.0	61.0	61.0	0.0	70.0	70.0	3.0	58.0	61.0	5.1	38.0	43.1	2.7	10.6	13.3

^a Hops in cold storage for one year.

COMPARISON OF THE ACID, ESTER, AND SAPONIFICATION NUMBERS OF THE FRACTIONS

The acid numbers of the fractions during each year are most variable; hence difficulty is encountered in attempting a comparison of the oils by this means. From the table it is quite obvious that the oils which in their original conditions possessed free acidity (as indicated by the high acid numbers) show much more decomposition of esters with the liberation

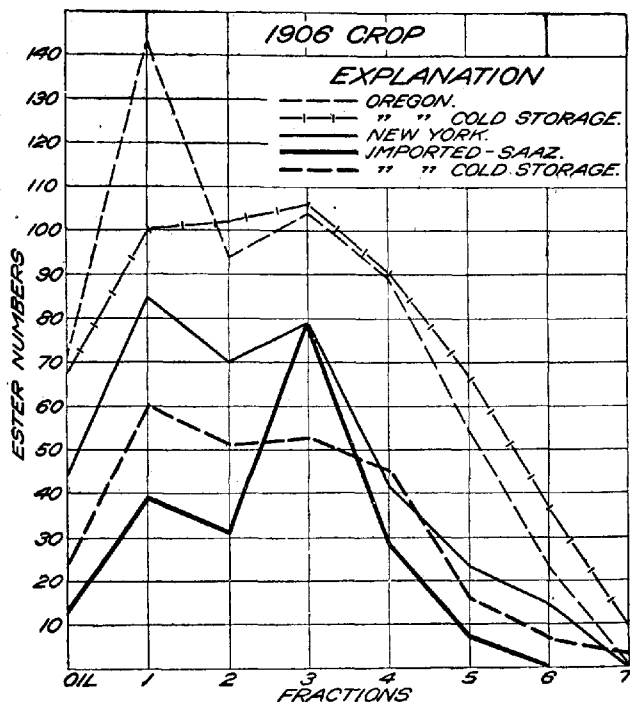


FIG. 10.—Ester-number curves of hop oils from the crops of 1906.

of free acids than do the oils with less acidity or with none. The acid numbers of the fractions of these high-acid oils are in all cases notably higher than those of similar fractions of the other oils. It is therefore very probable that oils with high acid numbers are much less stable than those free from acidity. This may in turn be true of the hops from which the oils were distilled. No particular oil appears to show a regular increase or decrease in acidity of the fractions, hence it is most difficult to draw conclusions from these values.

In direct contrast with the irregularity of the acid numbers of the various fractions there is a remarkable regularity of the ester numbers from year to year. There is also a most notable regularity of increase

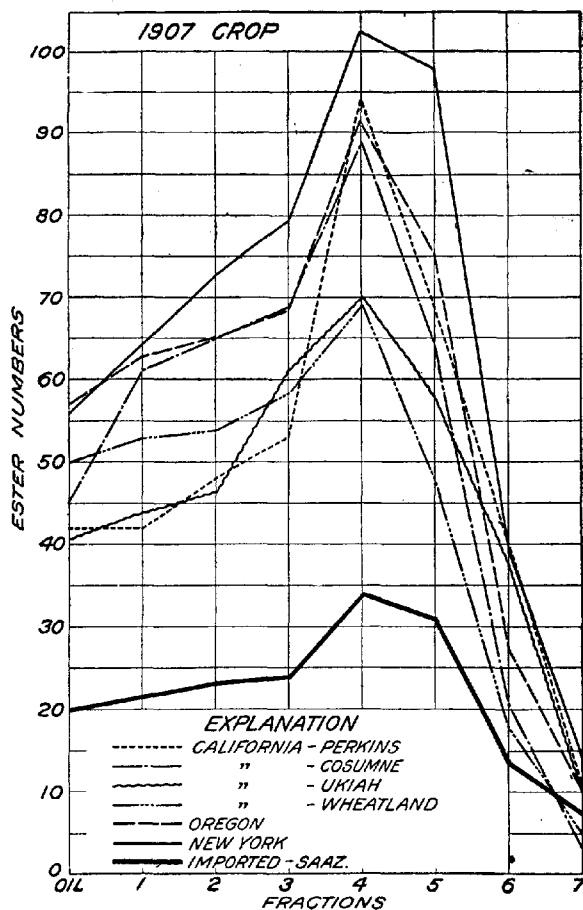


FIG. 11.—Ester-number curves of hop oils from the crops of 1907.

in ester numbers as the particular fractions are approached in which the boiling point most nearly corresponds to those of the esters present. A correspondingly regular decrease is noted in each succeeding fraction from this point to the highest boiling fraction. This is clearly shown by

the curves in figures 10, 11, 12, and 13. These curves show the ester numbers of the original oils and the fractions obtained from each oil, the general direction being the same in each season. Figures 11, 12, and 13 show the great similarity from year to year of the ester numbers and fractions of the oils from the same section. (See also fig. 1.) It will be

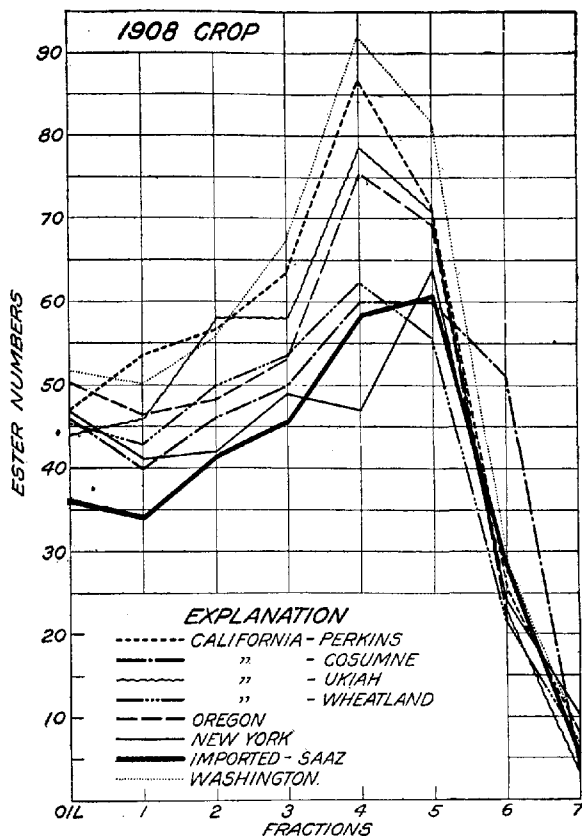


FIG. 12.—Ester-number curves of hop oils from the crops of 1908.

observed that a very close relationship exists between the oils and the fractions from any particular locality. The amount of esters increases as the fractionation proceeds until fraction 4 is reached, after which the quantity decreases until there is practically none in fraction 7. Apparently the oil highest in esters distills between the temperatures of 185° and

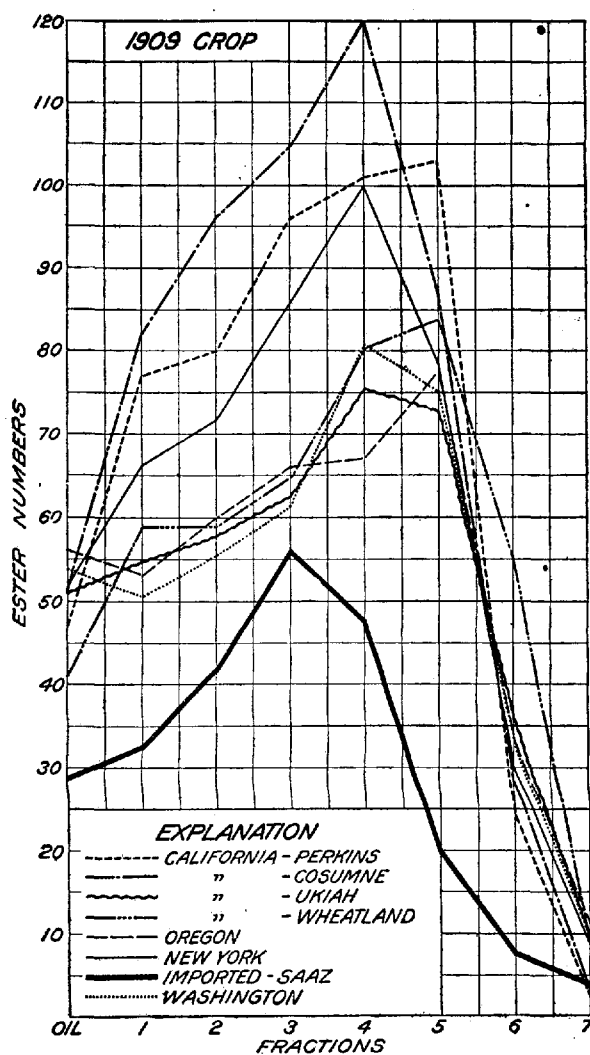


FIG. 13.—Ester-number curves of hop oils from the crops of 1909.

225° C., a considerable amount of esters, however, appearing also in the preceding fractions.

That the fractionation proceeded with fair regularity in each oil is shown by the relationship between the ester numbers of each fraction and the general direction of the curves, which is the same in all the oils.

During the three seasons the curves seem to group themselves according to the source of the hops, those of the oils which differ most in ester content being separate from the others. The course of the curves is therefore, in a sense, an indication of the source of the hops. Throughout the several seasons the curve of the imported hops is conspicuous by its low position as compared with the curves of the oils from the American hops. While it can not be stated with certainty that the oil from the imported hops would continue to show this low ester content, it is very probable that the same differences would continue, since nine samples from five successive seasons all yielded oils poorer in esters than the oils from the American hops during the same seasons.

CHEMICAL EXAMINATION OF THE OIL

FREE ACIDS

A small amount of free acids is contained in the oil of hops. In order to identify, if possible, these free acids, the oil was shaken out with an aqueous solution of sodium carbonate. The alkaline liquid was subsequently acidified and distilled with steam. The aqueous distillate, which was acid to litmus paper, was neutralized with sodium hydroxide and precipitated with silver-nitrate solution. By ignition of the dried silver salts, traces of formic and heptioic acids were observed, but the bulk of the volatile acids was identified as valerianic acid, 52 per cent of silver salt being obtained. (Silver valerianate requires 51.6 per cent of silver.) Formic acid was further identified by the formation of a silver mirror from ammoniacal silver-nitrate solution and by the reduction of mercuric chloride to mercurous chloride.

COMBINED ACIDS

After saponifying a quantity of the oil with alcoholic potassium hydroxide, diluting with water, and separating the unsaponified portion of the oil, the resulting alkaline liquid was evaporated to a small volume. Acidification with sulphuric acid caused the separation of an oily layer on the surface of the liquid. The oily acids thus separated had a pronounced odor of some of the higher fatty acids. After separation of the oily layer from the aqueous distillate by means of a separatory funnel, the distillate was shaken out with ether to remove traces of the insoluble fatty acids. The liberation of such a large quantity of oily acids shows that the esters of the oil are for the most part in combination with acids of a higher molecular weight which are oily in character and are sparingly soluble in water.

After neutralization and fractional precipitation with silver-nitrate solution, the aqueous distillate representing the soluble volatile combined acids produced small amounts of silver salts which contained 66 and 71 per cent of silver, respectively. The combined soluble acids therefore consisted largely of formic acid with a trace of acetic acid.

The oily acids previously mentioned, which represented the bulk of the combined acids, corresponded to 5 per cent of the total oil saponified. A small amount of the oily acids, which had a most unpleasant, repulsive odor, was neutralized with potassium-hydroxid solution. The neutralized solution was then precipitated fractionally with silver-nitrate solution. The first two fractions precipitated, which were the smallest and represented the most insoluble salts, yielded 38.5 and 39.2 per cent of silver, corresponding to decylic (caprinic) acid. (Silver salt of decylic acid contains 38.6 per cent of silver.) The third and fourth fractions of silver salts assayed 40.3 and 40.9 per cent of silver. These results correspond very closely to nonoic (pelargonic) acid, whose silver salt contains theoretically 40.7 per cent of silver. Fractions 5 and 6, containing 41.6 and 44 per cent of silver, respectively, had perhaps traces of the preceding nonoic and succeeding lower acids. In all probability a portion of these fractions consisted of octoic (caprylic) acid, which theoretically requires 42.9 per cent of silver. The final fractions both gave 46 per cent of silver, which corresponds well with heptoic (œnanthylic) acid. This acid contains theoretically 45.5 per cent of silver. Based on the total weight of all precipitates, it appears that the oily acids in combination as the esters in the oil of hops consist of about equal proportions of heptoic, octoic, and nonoic acids, with a somewhat smaller content of decylic acid.

Analyzing the fractions of a fractionated oil in another experiment for both free and combined acids, these results were verified in every respect, and additional acids were identified. In the lower boiling fractions butyric acid was identified among the free acids in addition to the formic, valerianic, and heptoic acids previously mentioned.

Heptoic, octoic, and nonoic acids were formed in the free state in the higher boiling fractions, due probably to the splitting off of these acids from the esters at the high heat of distillation. The insoluble acids in all the fractions consisted largely of heptoic and nonoic acids, with some octoic acid, the highest boiling fractions containing two higher acids, decylic and undecylic.

FRACTIONATION OF SAPONIFIED OIL

The saponified oil remaining after separation of the acids was twice fractionated with a 3-bulb Ladenburg flask, and the results are given in Table VIII.

TABLE VIII.—Fractionation of saponified oil of hops, showing physical properties of the fractions.

Fraction.	Temperature. ^a	Distilled over.	Specific gravity at 22°C.	Rotation in 50-mm. tube.	Refraction ND 22°C.	Remarks.
	°C.	Per cent.		Min.		
1.....	Below 160	4.0	0.8096	-21.7	1.4615	A large portion of this fraction distilled below 100°C. Strong irritating odor.
2.....	160 to 165	15.5	.8180	-21.7	1.4710	Mild aromatic, pleasant yet peculiar odor, unlike any of the common terpenes.
3.....	165 to 170	15.0	.8093	-23.9	1.4703	
4.....	170 to 175	2.7	.8440	-28.0	1.4750	Pleasant odor, similar to preceding fraction.
5.....	175 to 185	2.2	.8504	-33.2	1.4752	More strongly aromatic, pleasant.
6.....	185 to 195	2.1	.8767		1.4799	Distilled largely at 195°C. Pleasant hoplike odor.
7.....	195 to 205	.9			1.4836	Distilled uniformly. Pleasant odor, reminding of hops.
			.9060	-45.6		
8.....	205 to 215	.7			1.4865	Distilled mostly from 205° to 210° C. Odor pleasantly aromatic, less fragrant.
9.....	215 to 245	2.2	.8680	-45.6	1.4878	Temperature rose rapidly to 245° C. Odor less pleasant.
10.....	245 to 255	2.7	.8860	-23.9	1.4878	Distilled uniformly. Odor strong and rather disagreeable.
11.....	255 to 265	5.3	.8740	- 2.1	1.4871	Distilled uniformly. Odor strong and unpleasant.
12.....	265 to 275	6.0	.8850	+10.3	1.4947	Distilled largely between 265° and 270° C. Not strongly aromatic, disagreeable.
13.....	275 to 285	3.2	.8870	+ 6.9	1.4948	Disagreeable odor.
14.....	285 to 295	3.8	.8930	+ 7.6	1.4973	Heavy oil with rather strong, unpleasant odor.
15.....	295 to 305	2.8	.8940	+ 8.2	1.5000	Heavy oil with repulsive odor.

^a Residue 305° and over.

ALDEHYDE CONSTITUENTS

The initial distillate, which had a most irritating and penetrating action upon the nasal passages, was tested for reducing properties. A silver mirror was readily produced with silver nitrate, and a decolorized solution of fuchsin (magenta solution) became bright red immediately. Lebbin's solution (5 per cent resorcin in a solution of 40 to 50 per cent of sodium hydroxid) produced a deep-red color, characteristic of formaldehyde.

IDENTITY OF TERPENE HYDROCARBON WITH MYRCENE

The boiling points of the second and third fractions signified a terpenic character, but the odor was unlike that of the usual terpenes. An elementary analysis gave the following results:

Fraction 2.—Carbon, 87.5 per cent; hydrogen, 10.7 per cent.

Fraction 3.—Carbon, 86.4 per cent; hydrogen, 11.9 per cent.

While it must be remembered that these fractions were not pure, the percentage of carbon and hydrogen nevertheless points to terpene composition, since $C_{10}H_{16}$ requires 88.1 per cent of carbon and 11.7 per cent of hydrogen.

Preparation of the nitrosochlorid and other crystalline terpene derivatives with bromin and halogen acids failed in all cases. This, together with the unusually low specific gravity, pointed to another class of related hydrocarbons belonging to the aliphatic series. Aliphatic hydrocarbons with the same empirical formula, $C_{10}H_{18}$, are termed the "olefinic terpenes." The presence of olefinic terpenes in volatile oils was first observed by Power and Kleber (1895), who isolated a hydrocarbon from oil of bay, which was termed "myrcen." Chapman (1903) mentioned this hydrocarbon as a constituent of oil of hops.

In order to compare the hydrocarbon myrcene of bay oil with the hydrocarbon from hop oil, the properties of the respective compounds were tabulated as given in Table IX.

TABLE IX.—Comparison of the properties of hydrocarbon from oil of hops with the olefinic hydrocarbon myrcene.

Properties.	Hydrocarbon from oil of hops.	Myrcene.
Boiling point.....	165° to 170° C.....	171° C.
Specific gravity.....	0.8093 at 22° C.....	0.8023 at 15° C.
Index of refraction.....	1.4703.....	1.4673.
Rotation (50-mm. tube) ..	-23.9'.....	Inactive.
Color and behavior on standing.	Colorless, becoming slightly yellow and changing to a viscous mass.	Colorless, becoming yellow and resinifying.

A very close relationship is observed between the boiling point and the specific gravity of the two compounds. The slight discrepancies which exist, especially in the rotation, are probably due to some impurity of the fraction. The most striking characteristic of the hydrocarbon is its instability. The tendency to polymerize was most marked, the respective fractions in the large number of oils fractionated becoming viscous and almost solid in a comparatively short time. This peculiar property was observed by Power and Kleber (1895) in their experiments with the hydrocarbon from bay oil. It was also exhibited in oil of hops, which became viscous, even when the usual precautions were taken against light and air.

Since the properties of the hydrocarbon from the oil of hops show such a close resemblance to those of myrcene, it can be stated with comparative certainty that the terpene hydrocarbon, which represents the large proportion of the lower-boiling constituents, is identical with the olefinic terpene myrcene. By reference to the curves of fractionation of the various oils (figs. 2, 3, 4, and 5) it will be observed that in practically all cases myrcene constitutes the largest portion of the oils.

IDENTITY OF ALCOHOL AND ESTERS OF HOP OIL WITH MYRCENOL AND ITS ESTERS

If present in the oil, oxygenated constituents should have a tendency to concentrate themselves in the fractions above the temperature of 185°C . Therefore fractions 6, 7, and 8 were analyzed in order to determine their elementary composition. Granting that the separation of constituents is at most only partially effected by fractionation, the determination of the carbon and hydrogen content of these fractions should show the presence or absence of oxygenated compounds. The oxygenated compounds of a saponified oil are usually alcohols of the formula $\text{C}_{10}\text{H}_{18}\text{O}$. The fractions in question gave the following results:

Fraction 6.—Carbon, 81.7 per cent; hydrogen, 11.1 per cent.

Fraction 7.—Carbon, 80.0 per cent; hydrogen, 10.6 per cent.

Fraction 8.—Carbon, 81.4 per cent; hydrogen, 11.3 per cent.

$\text{C}_{10}\text{H}_{18}\text{O}$ requires 77.8 per cent of carbon and 11.7 per cent of hydrogen. The somewhat higher carbon content of the fractions may be explained by the fact that adhering traces of hydrocarbons were not completely separated in the earlier fractions. Oxygenated constituents of the nature of alcohols with the composition $\text{C}_{10}\text{H}_{18}\text{O}$ are strongly indicated in the fractions mentioned.

Since Barbier (1901) states that myrcene is capable of being hydrated chemically with the formation of an alcohol $\text{C}_{10}\text{H}_{18}\text{O}$, called "myrcenol," it was thought that the alcohol of hop oil might be allied to this compound. Furthermore, it is possible that an alcohol like myrcenol could occur in company with the terpene myrcene, from which it is capable of being prepared.

For a further comparison of the above fractions with myrcenol, Table X was prepared.

When it is remembered that the fractions contain admixtures of other constituents incapable of being separated by fractionation, the properties of the fractions compare very favorably with those of myrcenol. Sufficient similarity exists among the various properties, especially the boiling point, specific gravity, and refraction, to indicate the presence of an alcohol similar to myrcenol in the fractions recorded.

In this connection it was deemed advisable to call attention to the esters of the oil of hops, which are present in considerable proportion, and to compare the chief ester fractions of the oil with the acetic ester of myrcenol. As the fractionation of the oil proceeded, it was observed that the esters concentrated themselves in the fractions boiling at 185° to 225° and 225° to 260°C . Although the fractions were by no means pure esters, a comparison of the physical properties with those of the known esters of myrcenol shows that the esters of the oil boil at much higher temperatures than free alcohol. This is readily explained when

cognizance is taken of the fatty acids identified, whose boiling points are exceedingly high. Thus the boiling point of heptioic acid is 221° , of octoic acid 237° , and of nonoic acid 253° C. A combination of these acids with myrcenol, which boils at 213° to 215° C., would tend to produce esters with a boiling point much higher than the alcohol itself. The comparison of the chief ester fractions of hop oil with the acetic-acid ester of myrcenol is given in Table XI.

TABLE X.—Comparison of the physical and chemical properties of alcohol fractions from hop oil with the alcohol myrcenol.^a

Boiling points of hop oil fractions and myrcenol.	Specific gravity at 22° C.	Rotation in 50-mm. tube.	Refraction at 22° C.	Description.
Alcohol fractions from hop oil:				
185° to 195° C.	0.8767 b. 0.9060	a-45.6	1.4799	Nearly colorless; oily liquid with pleasant hoplike odor, becoming viscous on standing.
195° to 205° C.			1.4836	Slightly yellowish liquid with characteristic hop aroma, becoming viscous on standing.
205° to 215° C.			1.4865	Heavy yellowish oil with agreeable odor of hops, becoming very viscous on standing.
Myrcenol, 213° to 215° C. (99° to 101° C. at 10 mm.).	c. 0.9012		c 1.4778	Colorless oily liquid, very odorous; polymerizes, slowly becoming viscous.

^a Rotation of combined fractions, 185° to 215° C.

^b Specific gravity of combined fractions, 195° to 215° C.

^c At 14.5° C.

TABLE XI.—Comparison of the chief ester fractions of hop oil with the acetic-acid ester of myrcenol.

Fractions and ester of myrcenol.	Boiling point.	Description.
Chief ester fractions from hop oil:		
Fraction 4.	185° to 225° C. ...	Slightly yellow oily liquid with agreeable hoplike odor.
Fraction 5.	225° to 260° C. ...	Pale brownish liquid with strong hop odor.
Myrcenyl acetate.	^a 231° C.	Colorless oily liquid with strong odor.

^a 119° C. at 10 mm.

It is very probable that esters of the higher acids, as heptoic, octoic, and nonoic, would boil at higher temperatures than myrcenyl acetate. This would necessitate the concentration of the esters in fractions, as shown above. Earlier fractions would also contain some esters, as would later fractions, since the association of lower and higher boiling compounds with the esters would modify their boiling points. In order to show that the esters constitute no small proportion of the oil, curves of fractionation were made of the original oil (containing esters) and the same oil after saponification of the esters (fig. 14).

The curves show directly opposite courses from each other between the temperatures 170° and 260° C. It was between these temperatures that the large proportion of the esters of the original oil distilled over.

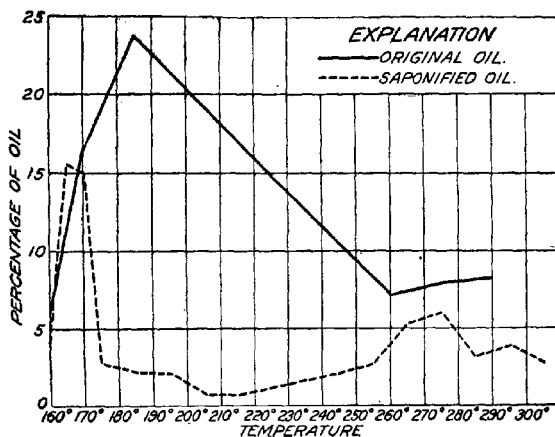


FIG. 14.—Fractionation curves of original and saponified hop oils.

It can therefore be readily perceived that a destruction of these esters by saponification and the consequent removal of the high-boiling acid portion of the esters would tend to flatten the curve of fractionation between these respective points.

The presence of the esters of myrcenol in the oil of hops is not surprising when it is known that the hydrocarbon myrcene, found in the low-boiling fractions, can be readily changed to myrcenol by the action of glacial acetic acid and dilute sulphuric acid. Myrcene bears the same relation to the alcohol myrcenol that camphor does to isoborneol and pinene or that dipentene bears to terpinol. It is very likely that the hydrocarbon myrcene is partly changed to myrcenol by hydration during the formation of the essential oil in the plant, the myrcenol in turn being esterified by the organic acids present.

The reason that it was impossible to quantitatively acetylate the oil was either because there was no free myrcenol present in the oil or because this alcohol would not acetylate without partial decomposition. The latter is probably the case, since in the experiments it was observed that the fractions containing the alcohol and esters were very unstable and readily polymerized to a viscous liquid. Furthermore, these fractions invariably gave negative results when acetylation was attempted.

IDENTIFICATION OF HUMULENE

Combustion of fractions 9 to 16 gave from 84 to 87.6 per cent of carbon and 11.2 to 11.8 per cent of hydrogen. The theoretical requirement of a sesquiterpene $C_{15}H_{24}$ is 88.1 per cent of carbon and 11.8 per cent of hydrogen. It is probable, therefore, that the fractions consisted of a sesquiterpene with inseparable quantity of alcohols, probably sesquiterpene alcohols which would have a tendency to lower the percentage of carbon. The hydrogen content would remain practically the same for the four classes of compounds—the terpenes, alcohols, sesquiterpenes, and sesquiterpene alcohols. Since the sesquiterpene humulene has been mentioned as a constituent of hop oil, a comparison was made between the physical properties of the high-boiling fractions of the saponified oil and the humulene obtained from different sources, the results being given in Table XII.

TABLE XII.—Comparison of the physical properties of high-boiling fractions of hop oil with those of humulene.

Properties.	Fractions of saponified hop oil.					Humulene.	
	255° to 265° C.	265° to 275° C.	275° to 285° C.	285° to 295° C.	295° to 305° C.	From hop oil. ^a 265° to 295° C.	From oil of poplar buds. ^b 265° to 269° C.
Boiling points of fractions and humulene.							
Specific gravity at 22° C.	0.8740	0.8850	0.8870	0.8930	0.8940	0.8987	0.8926
Rotation ^d	-2.1	+10.3	+6.9	+7.6	+8.2'	+1° 2'	+10° 48'
Refraction at 22° C. .	1.4871	1.4947	1.4948	1.4973	1.5000	1.4978

^a Chapman (1891).

^b Fichter and Katz (1899).

^c At 15° C.

^d Rotation of hop oil fractions determined in 50 mm. tubes.

^e 300-mm. tube.

Close relationship exists between the physical properties of the fractions of hop oil and those of humulene obtained from both oil of hops and oil of poplar buds. It is possible that traces of sesquiterpene alcohols occur in the fractions of the highest boiling points, since the boiling

points of certain sesquiterpene alcohols correspond very closely to these. Thus, cedrol, the sesquiterpene alcohol obtained from cedar-wood oil, boils at 282° , and santalol, obtained from oil of santal wood, boils at 301° C. The possible presence of sesquiterpene alcohols is also indicated by the low carbon content of these fractions, as shown by the elementary analysis. In order to positively identify the sesquiterpene humulene in oil of hops, three high-boiling fractions (225° to 245° , 245° to 260° , and 260° to 275° C.) of several unsaponified oils were used. Petroleum ether solutions of these fractions were treated with a concentrated solution of sodium nitrite with an equal volume of glacial acetic acid added in small portions and vigorously agitated, the mixture being kept well cooled. In fraction 245° to 260° there appeared blue needle-shaped crystals, which melted at 125° C. This is in accordance with the melting points of humulene nitrosite recorded by Chapman (1895b, p. 783) and by Fichter and Katz (1899), which are, respectively, 120° and 127° C. The characteristic blue coloration of the fraction from which the crystals were obtained was produced in each case.

APPROXIMATE COMPOSITION OF THE OIL

From the foregoing analysis of the oil of hops it appears that it has approximately the following composition:

FREE ACIDS.—Chiefly valericianic, with traces of formic, butyric, and heptic acids.

COMBINED ACIDS (*in form of esters*).—Chiefly heptic (α-nanthylic) and nonoic (pelargonic) and somewhat smaller quantities of octoic (caprylic), some decylic (caprinic) and undecylic acids, with traces of formic and acetic acids.

ALDEHYDES.—Formaldehyde in the lowest boiling fraction.

HYDROCARBONS.—Myrcene (olefinic terpene), 30 to 50 per cent. Humulene (sesquiterpene), 15 to 25 per cent.

ESTERS.—Chiefly heptic, octoic, and nonoic acid esters of the alcohol myrcenol, to the extent of 20 to 40 per cent. From the ester number (44) of the oil in question the amount of esters calculated as the heptic-acid ester of myrcenol was found to be 21 per cent. If calculated as the octoic or nonoic acid esters, the percentage would be considerably augmented.

ALCOHOLS.—Probably myrcenol and a small proportion of sesquiterpene alcohols.

RELATION OF THE VOLATILE OIL TO THE SOURCE OF THE HOPS

From the data presented it is clearly evident that the geographical source of hops has a pronounced effect upon the volatile oil and hence also upon the odor of the hops. The oils distilled from hops of different origin have been shown to possess like constituents, which, however, exist in sufficiently varying proportions to impart a decided difference to the properties of the oil. These differences appear to be constant from season to season, not only in the physical properties but also in the more important chemical properties. Most conspicuous among the chemical properties is the ester value, which is closely related to the odor. The ester content is the most influential factor in modifying the odor of the oils and

consequently that of the hops. It is usually acknowledged that hops of foreign origin possess a more agreeable odor than American hops. The difference in odor always seems to be perceptible although the odor is closely related to that of American hops. That the difference in odor is due to a difference in the volatile oil present can scarcely be questioned; in fact, it has been shown that such is the case. This is not, however, the only instance among aromatic plants where geographical source, with the different conditions of climate and soil, shows its effect in the differences in volatile oils distilled from the plants, as, for example, lavender and peppermint. Not only do hops of foreign origin produce oils noticeably dissimilar in some of their properties from the American oils, but hops grown even in separated sections of the United States have a different odor and yield oils with more or less constant differences from year to year.

CONCLUSIONS

The volatile oil of hops has been shown to consist chiefly of the terpene myrcene, the heptioic, octoic, and nonoic acid esters of the alcohol myrcenol, and the sesquiterpene humulene, with traces of free acids, formaldehyde, and probably some free alcohols. The constituents of chief importance as regards odor are the above-named esters, which constitute a large portion of the oil.

The several oils examined have been found to contain varying proportions of the esters as well as the terpene myrcene and the sesquiterpene humulene. Although no great importance can be attached to the two latter constituents, the variable content of esters is most significant, since the quality of the odor is probably most greatly influenced by them.

Important differences in the oils are apparent not only during any particular season but for several seasons. These constant differences are shown most forcibly in the curves of the physical and chemical properties of the oils. The curves of fractional distillation, which may be said to represent a partial quantitative separation of the chief constituents, bring out strongly the relationship which exists between the hops from any source during one season or several seasons. The optical rotation curves also show this relationship. In general the physical properties of the oils—the fractionation, specific gravity, and optical rotation—show strong similarities which may exist among related oils or strong dissimilarities among unrelated oils. The esters being regarded as the constituents of most importance in affecting the odor of the hops from which the oils were distilled are compared by means of the ester numbers. The curves of the ester content of the various oils and fractions of the oils show at a glance the remarkable differences in the oils from the several geographical sources. The curves followed by the imported oils are most conspicuous because of their constantly lower ester content. More remarkable is the fact that the ester content of the imported oils

remains lower from year to year, practically every sample under observation possessing an exceedingly low ester value. The oils from the California hops are both physically and chemically very similar from season to season. Those from the various sections of California show no important differences in their properties during any particular season, the curves showing considerable parallelism. The Oregon and Washington oils are very similar in their properties, but differ somewhat from the California oils. The New York oils seem to be the most closely related to the foreign oils in all properties, with the exception of the ester content, which is considerably higher. From the standpoint of the increasing ester content the various oils arrange themselves in the following order: Imported, California, Washington, New York, and Oregon, the three latter being very closely related. (See fig. 1.)

No general conclusions can be drawn regarding the possible superiority of any particular oil as compared with any of the other oils. Whether high or low ester content denotes richness or poorness in the quality of the hops, or vice versa, can not be definitely stated. Suffice it to say that from the results obtained it is clear that the geographical source of hops may be indicated by the ester numbers of the oil distilled from the hops, since the experiments show that the ester numbers of the oils from hops of any particular source or season are very similar.

REVIEW OF PREVIOUS CHEMICAL INVESTIGATIONS OF THE AROMATIC CONSTITUENTS OF HOPS

Reference to the odor of hops was made in literature as early as 1819. Loiseleur Deslongchamps (1819) mentioned the cones of hops as possessing a bitter taste and a strong odor resembling garlic. Hanin (1819) reported that the yellow powder of hops was very tasteful, very odorous, and inflammable, with all the characteristics of a resin. Ives (1821) in an investigation of the properties of hops, referred to the yellow powder of the cones as "lupulin," which, he stated, contained the bitter principle and the aromatic flavor of the hops. Working with samples of 1 dram to 2 ounces of lupulin, no volatile oil was separated, but the aqueous distillate possessed the odor of hops. The following year Payen and Chevalier (1822) found that by distilling the yellow powder (lupulin) a volatile oil was obtained which had the characteristic odor of hops.

The first investigation concerning the nature of the oil was made by Wagner (1853) who distilled the oil directly from the hops instead of from the lupulin. The oil was described as being bright brownish yellow in color with a strong odor of hops and a burning, slightly bitter taste. The solubility of the oil in water was sufficient to impart a decided hop odor, the solubility being influenced by dextrin, sugar, hop extract, etc. It was stated that the oil contained a terpene, which was likened to camphene, and also an oxygenated constituent, isomeric with borneo camphor.

According to Personne (1854), lupulin when boiled with water produced a volatile oil and a nonvolatile residue. Valerianic acid was identified among the volatile products; also an oxygenated compound called "valerol." Some years later Kuhnemann (1877) distilled hops with steam and obtained an oily substance which he called "hop oil." The oil was described as being a mixture of hydrocarbons and oxygenated compounds, the latter consisting of alcohols and acids. Ossipow (1883)

distilled commercial lupulin and obtained an oil. By experimenting with the oxidation of the oil he identified acetic and isovaleric acids. Octoic, or caprylic, acid was identified in the aqueous distillate from the oil by means of the silver salt. In the aqueous distillate from the lupulin he also identified butyric and valeric acids (1886).

It was not until 1893 that Chapman (1893) undertook the study of hop oil and obtained some insight regarding its actual composition. He found in his first experiments that an oil which had been standing for 11 months boiled considerably higher than freshly distilled oil and contained a sesquiterpene as its chief constituent. Continuing his work on the composition of the oil, he concluded after careful fractionation that the sesquiterpene which he had found as the chief constituent was humulene (1894; 1895a). The highest boiling fraction (263° to 266° C.), which consisted chiefly of humulene, represented in most cases about 40 per cent of the oil. The lowest boiling fraction (about 170° C.) also represented a large proportion of the oil and was considered to be a terpene hydrocarbon. The middle fractions had a pleasant odor and consisted of oxygenated compounds. The humulene from the highest boiling fraction of the oil was subsequently investigated by Chapman (1895b) and several crystalline derivatives of this compound were prepared. In a later report (1898) he stated that the oil contained no phenols, aldehydes, or ketones; that it was sparingly soluble in water, but sufficiently so to impart a characteristic odor to the water; also that the oil changed in the air to a viscous mass. In 1903 the investigation was continued (Chapman, 1903), and the lowest boiling fraction (166° to 168° C.) was found to have properties similar to myrcene from oil of bay. One of the higher boiling fractions had a strong odor, which fraction, it was stated, probably contained linalool or esters of linalool. The acids obtained by saponification of the oil were identified by means of their silver salts as valeric and isonononic acids. In all freshly distilled samples of the oil, myrcene and humulene were said to be present to the extent of 80 to 90 per cent.

Semmler and Mayer (1911) by the preparation of a number of characteristic derivatives established the identity of the terpene from hop oil with the terpene myrcene.

According to Deussen (1911) the humulene of hop oil is very similar in general properties and crystalline derivatives to the sesquiterpene caryophyllene.

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PRELIMINARY AND MINOR PAPERS

LESSER BUD-MOTH

By E. W. SCOTT and J. H. PAINE,

Entomological Assistants, Deciduous Fruit Insect Investigations,
Bureau of Entomology

During the spring of 1912, while engaged in apple spraying experiments at Benton Harbor, Mich., the senior author noticed the work of a small larva in the buds of unsprayed apple trees. The injury inflicted was severe in a neglected orchard near the laboratory, and this insect, among others, was the most important factor in the destruction of the entire crop of fruit. Because of the character of the injury, the attack on the swelling buds, and the tying together of the growing leaves, the damage was at once attributed to the eye-spotted bud-moth (*Imetocera ocellana* Schiff.).

In 1913 a study was made of the life history and habits of this insect, presumably the eye-spotted bud-moth, and experiments with remedial measures were tried. The first discrepancy noticed between the habits of this insect and those of the eye-spotted bud-moth, as recorded in literature, was the fact that the hibernacula were not necessarily situated near the buds, but were to be found in any suitable place upon the limbs. Following this, many other even more striking differences in habits were noted during the course of the season, and the fact was soon impressed upon the writers that they had to deal with an insect whose economic importance had not been recorded in the United States.

The adult moths, upon submission to August C. Busck, of the Bureau of Entomology, were identified as *Recurvaria crataegella* Busck (1903),¹ a species described by him (with no indication of its life history) in 1903 from material submitted by Mr. William Dietz, of Hazleton, Pa., who reared it from hawthorn (*Crataegus tomentosus*). At that time, however, Busck admitted the probability of the identity of his *R. crataegella* and the *R. nanella* of European authors.

Our own observations of the life history of the lesser bud-moth correspond in detail with those of Houghton (1903), who published a short though complete account of the life history of *Recurvaria nanella*. The *R. crataegella* of Busck is therefore to be regarded as a synonym of *R. nanella*, and in support of this decision Busck has recently furnished the following statement:

Recurvaria crataegella Busck (Proc. U. S. Nat. Mus., v. 25, p. 811, 1903) is identical with the European *R. nanella* Hübner, as already suggested in the description. At that time the life history of the species was but fragmentarily known in Europe, and it was deemed the soundest course to give the American form a separate name, even though it was realized that it would probably prove the same as the European species. The subsequent careful study of the life history in Europe by J. T. Houghton and in this country removed all doubt about the synonymy.

¹ Bibliographic citations in parentheses refer to "Literature cited," p. 162.

Stephens (1834) recorded *Recurvaria nanella* as "not very uncommon in gardens within the metropolitan district, frequenting the trunks of apple trees in June and the beginning of July."

Stainton (1854) recorded the larva as feeding in May on the pear, making a gallery across the flowers with pieces of the petals and stamens interwoven with silk.

Rössler (1871-72) observed the tying together of the young leaves of fruit trees by larvæ of *Recurvaria nanella* and its effect in hindering the development of the new leaves. The insect was present in such large numbers as to attract the attention of the public to the deformed trees and to arouse the fear that serious harm would result. In view of the fact that the larva was so small, ate so little, and did not attack the blossoms, Rössler considered that it was not to be feared.

Houghton (1903) published an account of the life history and habits of *Recurvaria nanella* from an economic point of view, as observed by him in England. His attention was directed to the insect in an apricot orchard, where the crop had been practically destroyed by it in previous years. He was the first to note the fact that the larva, after hatching, passes the time before hibernation as a miner in the leaf. He also observed that it was the habit of the larvæ to bore into the swelling buds in the spring. The larvæ appeared in swarms on peaches and apricots and less commonly on cherries and plums. He mentions the different colors assumed by the caterpillars as they near maturity, and this observation corresponds with our own.

The distribution of *Recurvaria nanella* in Europe is given by Staudinger and Rebel (1901) as follows: Central Europe, Sweden, northern Spain, southern France, central and northern Italy, Dalmatia, and southwestern Russia.

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TWO NEW WOOD-DESTROYING FUNGI

By JAMES R. WEIR,

Forest Pathologist, Investigations in Forest Pathology,
Bureau of Plant Industry

The opportunities afforded by the regular six months' field season, pursuant to the investigations in forest pathology in the great forest areas of the Northwest, have enabled the writer to collect the fungi of these regions with considerable completeness. In checking up the characters, affinities, and host relationships of a large number of species of wood-rotting fungi collected during the season of 1913 throughout Washington, Idaho, Oregon, and British Columbia, some new and highly interesting fungi, not heretofore reported, have come to light. Brief descriptions of the distinguishing features of two of these species follow.

Fomes putearius, n. sp.—Sporophores hard, woody, very irregularly lobed, recurving, slightly concave to applanate, occasionally broadly spreading to typically resupinate. The resupinate sporophores are often a foot or more in length. Pileate forms 12 to 14 by 6 to 8 by 0.4 cm. The surface in young specimens is velvety or tomentose, later becoming slightly encrusted, but always more or less corky, zonate, much wrinkled and furrowed in old age, in color deep brown, becoming darker; margin lighter colored, undulate, tomentose, thin, with narrow sterile border when young, later becoming thickened, rounded, and recurved by the successive annual layers; context corky to woody, thick deep brown; tubes irregularly but distinctly stratified 2 to 3 mm. long each season, but much longer in resupinate forms, brown; mouths uniformly oval, varying in size, 4 to 8 to a millimeters, edges thick, ferruginous; spores colored, globose, smooth, 7 to 8 μ ; spines dark brown, slightly ventricose 13 to 25 by 6 μ .

This fungus (Pl. IX, fig. 1), in addition to certain well-defined characters of the sporophore, is chiefly distinguished from its nearest relatives by its most remarkable rot and its host relationships. The fungus is closely related to *Fomes conchatus* (Pers.), which is always found on the wood of deciduous trees, especially on oaks (*Quercus* spp.) and willows (*Salix* spp.). Although many fungi show no discrimination between frondose and coniferous wood, *F. conchatus*, so far as the writer is aware, has not been reported on the wood of conifers, nor has it been collected in the West. Several collections at hand from southern Germany are all on the wood of broad-leaved trees. *Fomes putearius*, on the other hand, always occurs on coniferous wood, with a preference for larch (*Larix* spp.). The rot produced is one of the most conspicuous found in the northwestern forests and has determined the name of the fungus. The decomposition of the wood is quite similar to that produced by *Trametes pini* Fries, but the lignin reduction is on a much greater scale. The cellulose pockets produced by *F. putearius* are frequently more than 2 inches in length and vary in breadth according to the structure of the host. A common type of the rot in larch is shown in Plate IX, figure 2. In yellow pine (*Pinus ponderosa*) the pockets are smaller and more oval (Pl. IX, fig. 3); in Douglas fir (*Pseudotsuga taxifolia*) they are broadly oval (Pl. IX, fig. 4), while in Engelmann spruce (*Picea engelmanni*) they are smaller than in any of the other hosts. This is

clearly shown in Plate IX, figure 5, where the successive stages of the rot in this host are illustrated. The illustrations show the cellulose pockets in their natural size. As in case of other wood-destroying fungi, the rot varies to a limited extent, according to the anatomy and chemical contents of the wood of the host.

The rot produced by *Fomes conchatus* is entirely different. Conspicuous cellulose pockets are never formed, but the decay is frequently characterized by the appearance in close union of two distinct phases of the decomposition, depending, as it seems, on the physical and chemical nature of certain parts of the wood structure. A yellowish white rot first appears which may remain more or less permanently alongside other areas, continuing in the decomposition, later breaking up in irregular areas when dried.

The hard, black encrusting surface sometimes assumed by *Fomes conchatus* is never present in *F. putearius*. Neither does the context become as hard and woody. The spines, although present in considerable number in *F. putearius*, are not a conspicuous character. Those of *Fomes conchatus* are much more abundant and larger.

Type locality.—Priest River, Idaho; Kaniksu National Forest.

Habitat.—Dead coniferous wood.

Range.—Throughout the Northwest, most abundant in the white-pine zone.

Specimens have been examined from practically all the main forest regions.

Trametes setosus, n. sp.—Sporophores pileate or entirely resupinate, depending upon its position on the substratum. The resupinate forms have sharply defined sterile margins and are usually found on the underside of logs, where they may extend for a distance of a foot or more. The distinctly sessile pileate forms are usually free from each other, but may be connected by the resupinate portion, occasionally narrowed at the point of attachment, mostly thickened at the base, rarely applanate or conchate, averaging 1 by 2 by 2 cm. Surface minutely tomentose, becoming smooth or weathered in old specimens, zonate, rich dark brown, uneven; margin thick, of lighter color, entire, becoming slightly serrate in old age, slightly sterile; context ferruginous or fulvous, spongy to corky, slightly zonate, particularly in old specimens; tubes long, often filled with a grayish mycelium, 1 to 1.5 mm.; mouths small, mostly angular, occasionally labyrinth-like, 3 to 6 to a millimeter, edges thick, tomentose; spores hyaline, 4 to 5 by 3 μ . The character that distinguishes the species from all of its near relatives is the immense number of long dense brown setae lining the interior of the tubes. In no other species known to the writer is this character so distinctly pronounced. The longest spines measure 41.45 μ , the shortest about 22.16 μ , with an average of 30.46 μ . The nature and immense number of these setae may be determined by a study of Plate X, figure 11.

The fungus shown in Plate X, figures 6 to 11, was first collected in the Kaniksu National Forest near Priest River, Idaho, on fallen *Pinus monticola*. This tree is the principal host, although the fungus occurs occasionally on the wood of other trees but always on conifers. *Polyporus gilvus* Fr., which seems to be the nearest relative and is usually found on the wood of deciduous trees, has not, so far as the writer is aware, been collected in the West.

Trametes setosus, on account of its abundance, causes serious damage to fallen merchantable timber in forest-fire areas. The chemical action of the mycelium on the wood is to reduce the lignin principally in the spring wood, leaving a cellulose ring alternating with sound autumn wood (Pl. X, fig. 10), which causes the annual rings to separate.

Type locality.—Priest River, Idaho; Kaniksu National Forest.

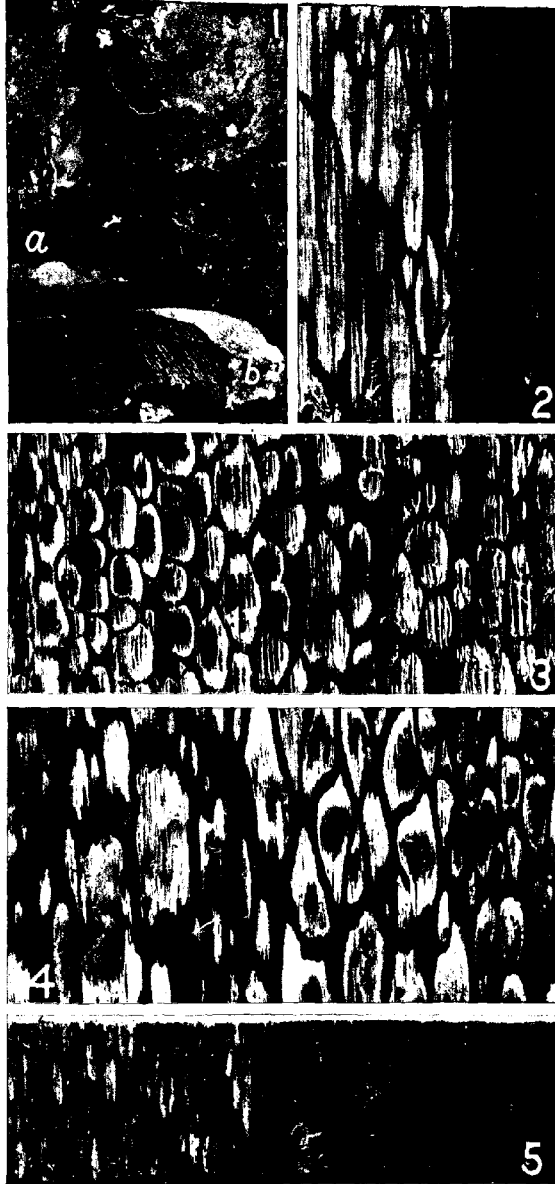
Habitat.—Dead coniferous wood.

Range.—Throughout the white-pine (*Pinus monticola*) belt of the Northwest. Specimens were collected in all the principal forest areas from Vancouver, B. C., to Montana.

Type specimens of both species have been deposited in the Office of Investigations in Forest Pathology and in the Pathological Collections of the Bureau of Plant Industry, Washington, D. C.

PLATE IX

- Fig. 1.—*Fomes putearius* from the wood of *Larix occidentalis*, showing a typical pilate fruiting structure; also a section through the resupinate form.
Fig. 2.—*Larix occidentalis*, showing decay of the wood by *Fomes putearius*.
Fig. 3.—*Pinus ponderosa*, showing disintegration of the wood by *Fomes putearius*.
Fig. 4.—*Pseudotsuga taxifolia*, showing the typical decay caused by *Fomes putearius*.
Fig. 5.—*Picea engelmanni*, showing the different stages of the decay caused by *Fomes putearius*.



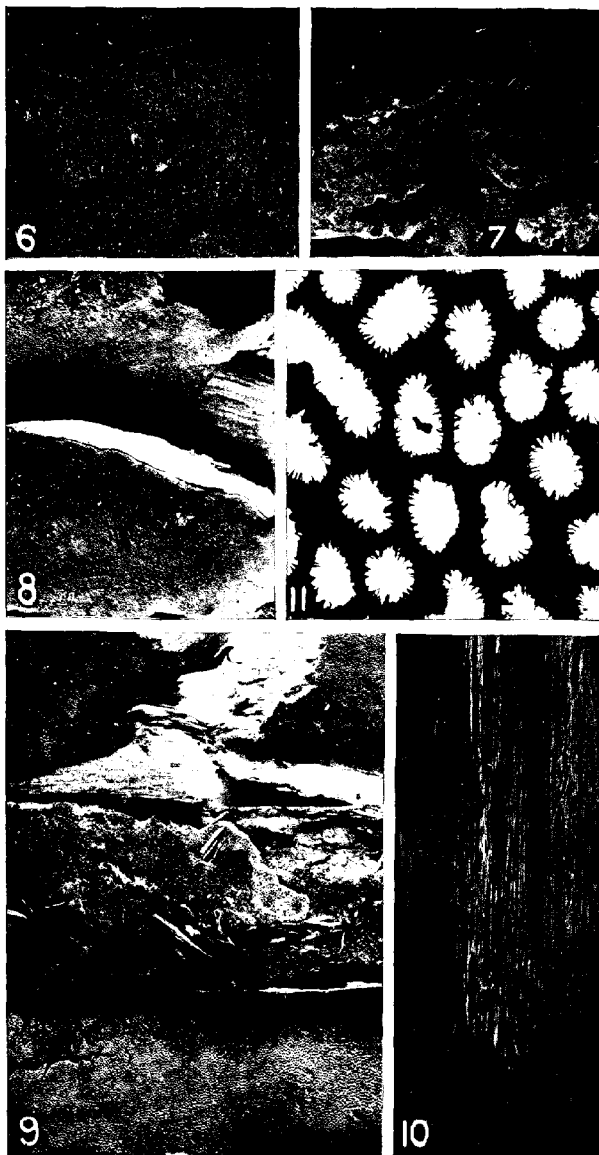


PLATE X

- Fig. 6.—*Trametes setosus* on *Pinus monticola*; resupinate form.
Fig. 7.—*Trametes setosus* on *Pinus monticola*; sessile pileate form.
Fig. 8.—*Trametes setosus*; common form on *Thuja plicata*; pores very slightly enlarged.
Fig. 9.—*Trametes setosus* on *Larix occidentalis*.
Fig. 10.—*Thuja plicata*, showing decay of the wood caused by *Trametes setosus*.
Fig. 11.—*Trametes setosus*: Transverse section of the pores showing the numerous setæ, $\times 60$.

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